291. *The Ignition of Gases. Part VIII. Ignition by a Heated Surface.* (a) *Mixtures of Ethane, Propane, or Butane with Air:* (b) *Mixtures of Ethylene, Propylene, or Butylene with Air.*

By C. A. Naylor and R. V. Wheeler.

(a) *Mixtures of Ethane, Propane, or Butane with Air.*

By the same method and with the same apparatus as was used for mixtures of methane with oxygen and nitrogen, argon, or helium (see Part VII; J., 1931, 2456 *), the relative ignition temperatures for series of mixtures with air of ethane (1—11%), propane (1—12%),

---

* Numbered Part VI in error.

and *n*-butane (1—10%) have been determined and are recorded graphically in Fig. 1 for two sizes of quartz reaction vessels: I, 48 c.c. (ratio, surface/volume 1·3) and II, 440 c.c. (ratio, surface/volume 0·6). The "lags" on ignition were: *Ethane*, vessel I, between 21 sec. (1·2% ethane at 608°) and 82 sec. (10·9% ethane at 539°); vessel II, between 30 sec. (1% ethane at 577°) and 742 sec. (9·9% ethane at 498°). *Propane*, vessel I, between 6 sec. (1% propane at 615°) and 24 sec. (12·05% propane at 529°); vessel II, between 20 sec. (0·9% propane at 551°) and 131 sec. (10·0% propane at 481°). *Butane*, vessel I, about the same, 14 sec., for all mixtures; vessel II, from 22 sec. (1·0% butane at 533°) rising to 32 sec. (3% butane at 490°) and then falling to 10 sec. (10·5% butane at 441°).

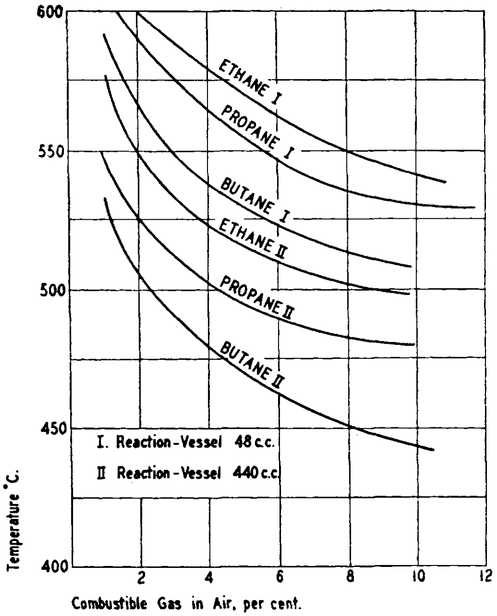
We have shown that the reactions between methane and oxygen (in admixture with an inert gas) resulting in the production of flame, when the mixture is admitted to a heated vessel, are thermal reactions catalysed by the products of an initial slow and flameless combustion. The present work deals with the reactions that occur, under similar conditions, with mixtures of ethane, propane, or butane with air. It is found that, although the reactions are of the same general character as with methane, yet there are important differences, namely:

(1) With mixtures of methane and air, the ignition temperature is lowest and the "lag" at that temperature is longest when there is excess of oxygen; whereas with the higher paraffins the lowest ignition temperatures and the longest "lags" at those temperatures are obtained when there is excess of the paraffin.

(2) At a given temperature higher than the ignition temperature, the "lag" with methane is shortest when there is excess of oxygen, and with the higher paraffins it is shortest when there is an excess of the paraffin (see also, "The Ignition of Gases, Part IV," J., 1924, **125**, 1869).

(3) With mixtures of methane and air, the reactions occurring below the ignition temperature are retarded by traces of iodine, ethyl iodide, or ethyl bromide; whereas with ethane the corresponding reactions are accelerated by these substances.

FIG. 1.



(4) With methane, the addition at the outset of small amounts of the intermediate products of oxidation, formaldehyde or carbon monoxide (or both), accelerates the reactions; whereas with ethane such additions have no appreciable effect.

We have studied the reactions that occur during the oxidation of the higher paraffins (more particularly ethane) preliminary to the production of flame within a closed vessel, by rapidly withdrawing samples of the gases for analysis after measured intervals of time, in the same manner as when dealing with methane (*loc. cit.*, p. 2459). The information so obtained enables an explanation to be given for the differences in behaviour enumerated.

The initial reactions with the higher paraffins, under the conditions of the experiments, include their thermal decomposition, with the formation of the corresponding olefin (see, in this connexion, Hague and Wheeler, J., 1929, 378), the ignition temperature of which is lower by 15—25° (see p. 1244). Mixtures of ethane, propane, or butane with air, therefore, are more readily ignited the greater the concentration of the paraffin; in contradistinction to the behaviour of mixtures of air with methane, which is thermally stable at its ignition temperature.

The effect on the (surface) reactions between methane and oxygen of extraneous substances such as iodine, is to retard them, and the effect is most pronounced when they are present in small quantities; whereas, with a mixture of ethane and air, such substances accelerate not only the surface reactions but also those that result in flame, the more so the greater their concentration. It would seem as though the oxidation of the products of decomposition were first accelerated, and that, in consequence, the rate of decomposition of the paraffin were then increased. Pease (*J. Amer. Chem. Soc.*, 1929, **51**, 1839) has shown that with mixtures of propane and oxygen decomposition of the hydrocarbon is excited by its simultaneous oxidation and, also, that it is necessary to approach the temperature for thermal decomposition before any oxidation occurs.

The reaction between ethane and oxygen at temperatures below the ignition temperature has been stated to be a chain reaction (see, *e.g.*, Bone and Hill, *Proc. Roy. Soc.*, 1930, *A*, **129**, 434). Such a reaction is usually characterised by a high temperature coefficient and, if explosion can occur, by a sudden transition from slow to explosive reaction. The reactions studied in the present research, with ethane and air, have low temperature coefficients which decrease with increase of temperature range. The values, obtained by assuming that the reciprocal of the " lag " on ignition affords an approximate measure of the rate of reaction, are :

Gas.	Temp. range.	*k* (average). 48-c.c. vessel.	*k* (average). 440-c.c. vessel.	Heat of activation, *E*, cals. 48-c.c. vessel.	Heat of activation, *E*, cals. 440-c.c. vessel.
Ethane	610—750°	1·19	1·15	31,000	25,000
Propane	600—800	1·17	1·11	30,000	19,000
Butane	560—750	1·14	1·10	22,000	16,000

The reactions are not isothermal. At or above the ignition temperatures of the mixtures, the rate of liberation of heat in the system exceeds the rate at which it is dissipated; the temperature rises and the increase of temperature causes the reactions to accelerate until ignition occurs. These are characteristics of thermal reactions.

It appears that when nitrogen is present, as in our experiments, the reactions between ethane and oxygen at temperatures below the ignition temperature are modified; for Bone and Hill (*loc. cit.*, p. 441) record the formation of both acetaldehyde and formaldehyde when $2C_2H_6 + O_2$ was heated at 303—305° or $C_2H_6 + O_2$ at 313—316°, whereas in none of our experiments (at 528° and 538°) could the presence of acetaldehyde be detected. Moreover, in our experiments the early formation of ethylene is important, whilst in those by Bone and Hill, none (or but a trace, presumably produced by the secondary decomposition of ethyl alcohol) could be detected; no doubt because their experiments were carried out at temperatures well below the decomposition temperature of ethane (*ca.* 460°).

EXPERIMENTAL.

The apparatus and method of experiment have been described in detail in J., 1931, 2456. Briefly, the reaction vessel was a cylindrical vessel of transparent quartz heated in an electric resistance furnace. One end of the vessel could communicate with either (*a*) a recording manometer, for registering the moment of ignition and the duration of the lag, or (*b*) an evacuated glass globe of 4-l. capacity, for rapidly withdrawing samples of the reacting gases; the other end was connected to the bell of a small gas-holder of special construction and hence to a vacuum pump. In carrying out an experiment, just sufficient of the chosen gas-mixture to fill the heated reaction vessel at atmospheric pressure was introduced into the gas-holder; the reaction vessel was then evacuated, and the mixture allowed to enter it rapidly by suitable manipulation of taps. Three reaction vessels were used, two, of 48 and 440 c.c. capacity, for determinations of ignition temperatures and " lags," and one, of 460 c.c. capacity, for studying the reactions during the " lag " period. The pure gases were obtained by repeated liquefaction and fractional distillation until the theoretical value *C*/*A* on explosion analysis was recorded. Each hydrocarbon was of 99·5% purity, the impurity being nitrogen.

In addition to determinations of the " lags " at the ignition temperatures of the various mixtures, their values at higher temperatures were measured. These are recorded in Table I.

These determinations confirm the evidence given by the records of ignition temperatures (Fig. 1), that the reactions resulting in flame are dependent on the concentration of the combustible gas, for the lag on ignition at each temperature is shorter the higher the proportion of ethane, propane, or butane present. The opposite effect was observed with methane (*loc. cit.*, p. 2460).

TABLE I.

Lags on Ignition of the Paraffins at Temperatures above their Ignition Temperatures (*secs.*).

Temp.	Ethane.			Propane.			Butane.		
	%.	Vessel I (48 c.c.).	Vessel II (440 c.c.).	%.	Vessel I (48 c.c.).	Vessel II (440 c.c.).	%.	Vessel I (48 c.c.).	Vessel II (440 c.c.).
600°	2·20	—	5·21	2·05	4·91	—	1·00	4·25	2·77
	3·65	17·8	3·85	3·05	—	2·39	1·75	2·43	2·22
	7·80	4·85	2·63	4·30	2·01	—	3·20	1·48	1·63
	8·70	3·55	2·47	5·05	—	1·90	5·05	1·18	1·38
	12·1	2·20	2·20	6·10	1·56	—	7·55	0·95	1·14
				8·05	1·36	—	10·40	0·85	1·06
				8·30	—	1·48			
				10·05	—	1·45			
				10·35	1·24	—			
650	1·10	3·25	2·44	1·00	1·58	1·72	0·85	1·16	1·36
	2·85	1·52	1·63	2·10	1·07	—	1·75	0·91	1·15
	6·70	1·00	1·17	3·05	—	1·13	2·55	0·77	0·97
	9·10	0·87	1·01	4·30	0·78	—	4·75	0·63	0·77
	12·55	0·71	0·86	4·90	—	0·94	7·15	0·52	0·64
				6·05	0·70	—	9·90	0·47	0·57
				8·30	0·61	0·80			
				10·35	0·58	—			
				10·55	—	0·67			
700	0·90	0·92	1·17	0·95	0·69	—	0·95	0·59	0·74
	2·90	0·64	0·69	1·10	—	0·82	2·25	0·49	0·59
	7·05	0·50	0·50	2·10	0·57	—	4·90	0·39	0·44
	8·70	0·44	0·46	2·45	—	0·64	7·15	0·34	0·38
	12·10	0·35	0·40	4·10	0·43	—	10·10	0·31	0·35
				4·90	—	0·46			
				6·05	0·37	—			
				7·35	—	0·39			
				7·75	0·33	—			
				9·80	0·30	—			
				10·60	—	0·37			
750	0·90	0·44	0·53	0·95	0·39	—	1·15	0·33	—
	2·90	0·26	0·35	1·00	—	0·47	2·45	0·26	—
	6·70	0·23	0·26	2·00	—	0·40	3·65	0·23	—
	9·10	0·21	0·24	2·05	0·33	—	5·00	0·21	—
	12·55	0·20	0·21	3·55	—	0·32	7·65	0·20	—
				4·10	0·26	—	9·75	0·20	—
				6·10	0·20	—			
				7·75	0·19	—			
				9·55	—	0·25			
				9·75	0·18	—			

The Reactions during the Period of " Lag."—In a preliminary experiment, 40 l. of a 6% ethane–air mixture were passed slowly through the reaction vessel (460 c.c.) heated at 528°, and the products passed through (*a*) distilled water and (*b*) bromine. The aqueous solution was tested for alcohol, aldehydes, organic acids, and glycol, but only formaldehyde could be detected. The bromide formed was purified and found to be ethylene dibromide.

In other series of experiments, the contents of the reaction vessel were rapidly removed after successive charges of the same mixture had remained in the vessel during measured intervals of time. Temperatures of 528° (6·23% C_2H_6) and 538° (6% C_2H_6) were used, the " lags " at these temperatures being 230 and 91 sec. The results of analyses of the samples are recorded in Table II.

The percentages of formaldehyde and steam are calculated from the carbon and hydrogen balances. Tests for formaldehyde, with phenylhydrazine hydrochloride, potassium ferricyanide and hydrochloric acid (Schryver's reaction), were made on each sample with positive results. No acetaldehyde could be detected by trimethylamine and sodium nitroprusside, a test capable of showing 1 part of acetaldehyde in 10,000.

With mixtures of methane and air, the intermediate products begin to disappear as the reaction proceeds, and the previous addition of either formaldehyde or carbon monoxide accelerates the reaction. With ethane, however, it will be seen that the intermediate products, ethylene and formaldehyde, accumulate: the previous addition of either has relatively little effect, as the records in Table III show.

TABLE II.

Analyses of Gases during Period of Lag on Ignition.

(Ethane–air, 6·23% C_2H_6. Temp. 528°.)

Duration of heating, secs.	Analyses of gases, %.						
	CO_2.	O_2.	C_2H_4.	CO.	C_2H_6.	CH_2O.	H_2O.
4½	0·03	19·04	nil	0·29	5·92	0·30	0·60
30	0·03	18·38	0·24	0·28	5·48	0·71	1·06
60	0·07	19·11	0·43	0·25	5·54	0·20	1·01
90	0·11	17·47	0·51	0·22	4·74	1·63	1·82
121	0·13	17·97	0·67	0·39	5·00	0·60	1·75
200	0·14	17·92	1·31	0·58	4·33	0·46	2·62
228	0·34	15·64	2·06	1·80	2·63	0·94	5·74
	(6·00% C_2H_6. Temp. 538°.)						
15	0·03	19·54	0·37	0·37	5·40	0·06	1·00
34	0·12	19·10	0·53	0·06	5·13	0·50	1·05
45	0·09	18·44	0·98	0·16	4·69	0·41	1·56
60	0·17	18·29	1·00	0·40	4·54	0·35	2·03
76	0·15	17·35	1·16	0·44	—	—	—
90	0·65	16·03	1·87	1·44	2·90	0·37	5·19

TABLE III.

The Effect of Formaldehyde and Ethylene on the Lag on Ignition of Ethane–Air Mixtures.

Mixture with air.	Temp.	Lag, secs.	Mixture with air.	Temp.	Lag, secs.
C_2H_6, 6·05%	526°	260	C_2H_6, 5·8%; CH_2O, 0·05%	527°	187
C_2H_6, 5%; C_2H_4, 1%	526	190		537	97
C_2H_6, 5·8%	527	265	C_2H_6, 4·8%; C_2H_4, 1%; CH_2O, 0·05%	527	146
	537	99		537	67

The Action of Ethyl Iodide and Ethyl Bromide.—Experiments with mixtures of methane and air (*loc. cit.*, p. 2466) have shown that the addition of traces of iodine, ethyl iodide, or ethyl bromide elevates the ignition temperatures and decreases the rate of reaction at lower temperatures. With ethane and oxygen ($C_2H_6 + O_2$ at 316°) Bone and Hill (*loc. cit.*, p. 444) have found that the presence of iodine (1%) shortened an " induction " period of 30 minutes (during which, apparently, no reaction occurred) to 5 minutes, and a subsequent " reaction " period of 70 minutes to 25 minutes. We have found that the addition of traces of either ethyl iodide or ethyl bromide to a mixture of ethane and air accelerates the reactions at temperatures near the ignition temperature. The records given below illustrate this.

The Effect of Ethyl Iodide or Ethyl Bromide on the Lag on Ignition of a 5·8% Ethane–Air Mixture.

	Temp.	Lag, secs.		Temp.	Lag, secs.
No addition	527°	265	EtI, 0·20%	527°	23
	529	190		529	22
EtI, 0·03%	527	163	EtBr, 0·10%	529	73
EtI, 0·10%	527	59	EtBr, 0·20%	527	83
	529	36		529	38

For comparison with the results recorded in Table II, an experiment was made in which a 5·8% ethane–air mixture with 0·02% of ethyl bromide was heated at 527°, and the products were removed after 75 secs. The analysis showed: CO_2, 0·26; O_2, 16·85; C_2H_4, 1·66; CO, 1·45; C_2H_6, 2·89; CH_2O, 0·79; H_2O, 4·62%. If comparison is made, *e.g.*, with the samples withdrawn after 90 secs. when a 6·23% ethane–air mixture was heated at 528°, it will be seen that the reactions took the same course when a trace of ethyl bromide was present, but were much accelerated.

(b) *Mixtures of Ethylene, Propylene, or Butylene with Air.*

The ignition temperatures of the olefins have been found to be 15—25° lower than those of the corresponding paraffins. The lags at the ignition temperatures are shorter with ethylene or butylene than with ethane or butane, but are longer with propylene than with propane.

At the temperatures used in our experiments, the reactions between the olefins and oxygen resulting in the production of flame are thermal reactions catalysed by the products of an initial slow and flameless combustion. The rate of reaction is influenced more by the concentration of the hydrocarbon than by that of the oxygen. This fact, taken in conjunction with the results of previous experiments with the paraffins, suggests that as a first step in the oxidation of the olefins there is decomposition; or decomposition and oxidation may be simultaneous. This view is confirmed by the production of formaldehyde in considerable quantities during the pre-flame period.

The temperature coefficients for the reactions are low. Whereas with propylene the coefficient decreases with increase of temperature, it increases with ethylene and butylene, the increase being the more marked with ethylene. The approximate values for the temperature coefficients and the heats of activation with air between 600° and 750°, calculated on the assumption that the reciprocal of the " lag " on ignition affords a measure of the rate of reaction, are :

Combustible in air	Ethylene	Propylene	Butylene
k	1·174	1·146	1·117
E, cals.	29,000	25,000	20,000

Hinshelwood and Thompson (*Proc. Roy. Soc.*, 1929, *A*, **125**, 277) give for the heat of activation of ethylene with oxygen a value of 35,000—43,000 cals.

EXPERIMENTAL.

The ignition temperatures and lags on ignition have been determined in the manner previously described. The reaction vessel was of transparent quartz of 48 c.c. capacity. The results, which include determinations of the lags at different temperatures, are recorded in Tables IV and V.

TABLE IV.

Relative Ignition Temperatures of the Olefins in Air.

(Reaction vessel, 48 c.c. Ratio, surface : volume, 1·3.)

C_2H_4, %.	Ignition temp.	Lag at ignition temp., secs.	C_3H_6, %.	Ignition temp.	Lag at ignition temp., secs.	C_4H_8, %.	Ignition temp.	Lag at ignition temp. secs.
1·85	589°	4·1	1·65	582°	9·1	1·00	580°	4·6
2·30	581	5·5	3·40	550	18·6	2·10	548	6·8
2·90	572	5·8	4·00	542	21·0	3·10	529	8·2
4·50	559	4·9	5·95	524	32·6	4·05	517	8·0
5·85	552	8·1	7·95	510	43·3	5·10	502	9·8
6·70	547	13·2	9·85	504	50·8	5·85	496	10·9
7·70	541	12·0	11·70	499	62·2	7·30	488	10·7
8·75	536	11·0				8·20	485	10·5
9·95	531	9·5				9·20	484	9·6
10·65	529	8·0				10·10	480	10·4
11·00	528	—				11·10	478	9·8
12·80	523	8·8						

The Period of Lag.—A study of the reactions taking place during the pre-flame period was made by withdrawing samples of gas from the reaction vessel after given intervals of time in successive experiments and analysing them. A mixture containing 4·95% of ethylene in air was used in these experiments, the temperature of the reaction vessel being maintained at 540°. The ignition temperature of the mixture was 556°.

The analyses showed that, when the duration of heating did not exceed 70 secs., the principal products were carbon monoxide, formaldehyde, and steam, with smaller amounts of carbon dioxide and higher olefins. When the time of heating exceeded 70 secs., the higher olefins disappeared, whilst the quantities of the other products increased. The results of three representative analyses are given in Table VI.

The percentages of formaldehyde and steam are calculated from the carbon and hydrogen balances. Tests for formaldehyde were made during each experiment, and the results obtained confirmed those obtained from the analyses.

TABLE V.

Lags on Ignition of Olefin–Air Mixtures at Temperatures Higher than Their Ignition Temperatures.

(Reaction vessel, 48 c.c.)

Temp.	C_2H_4, %.	Lag, secs.
600°	2·60	2·16
	4·95	1·25
	6·95	1·07
	10·25	0·84
	13·80	0·70
	17·00	0·62
650	1·25	0·88
	2·85	0·69
	6·10	0·48
	8·55	0·39
	10·25	0·36
	12·00	0·34
	14·25	0·31
	17·90	0·27
700	1·40	0·39
	2·85	0·30
	6·10	0·22
	8·15	0·21
	10·95	0·17
	14·15	0·15
	17·60	0·12
750	1·20	0·17
	2·55	0·12
	5·00	0·11
	8·15	0·10
	10·95	0·09
	14·15	0·07
	16·00	0·06

Temp.	C_3H_6, %.	Lag, secs.
600°	1·90	4·28
	2·95	4·07
	3·70	4·00
	5·00	3·90
	6·50	3·84
	8·00	3·80
	9·60	3·78
650	1·00	1·68
	2·00	1·53
	2·95	1·46
	3·95	1·44
	5·20	1·39
	6·50	1·35
	7·70	1·34
	8·70	1·30
700	1·35	0·85
	2·00	0·82
	2·80	0·80
	4·10	0·79
	4·90	0·79
	5·90	0·77
	7·15	0·74
	8·35	0·73
	9·65	0·72
750	1·35	0·54
	2·95	0·49
	4·00	0·48
	5·25	0·44
	6·30	0·43
	7·85	0·43
	9·25	0·42
	10·75	0·42

Temp.	C_4H_8, %.	Lag, secs.
600°	1·05	1·68
	2·00	1·13
	2·40	1·06
	3·10	0·95
	4·25	0·83
	5·40	0·77
	6·75	0·72
	7·80	0·71
	9·05	0·70
	9·80	0·69
	10·45	0·68
650	1·00	0·75
	1·95	0·58
	2·90	0·49
	4·00	0·46
	4·90	0·43
	5·90	0·41
	6·95	0·40
	8·20	0·39
	9·20	0·39
700	1·15	0·38
	2·20	0·32
	3·50	0·28
	4·65	0·26
	5·65	0·24
	7·15	0·23
	8·25	0·23
	9·55	0·22
750	1·00	0·23
	2·00	0·18
	2·40	0·17
	2·95	0·15
	4·10	0·13
	5·45	0·13
	6·90	0·14
	8·10	0·14
	9·00	0·13
	9·80	0·13

TABLE VI.

Analyses of Gases during Period of Lag on Ignition.

(4·95% Ethylene in air. Temp. 540°.)

Duration of heating, secs.	Analyses of gases, %.					
	Higher olefins.	CO_2.	C_2H_4.	CO.	CH_2O.	H_2O.
30	0·13	0·19	2·79	2·18	1·25	2·47
70	0·24	0·28	2·06	2·95	1·57	3·23
90	nil	0·70	2·17	2·89	1·95	3·59

DISCUSSION OF RESULTS.

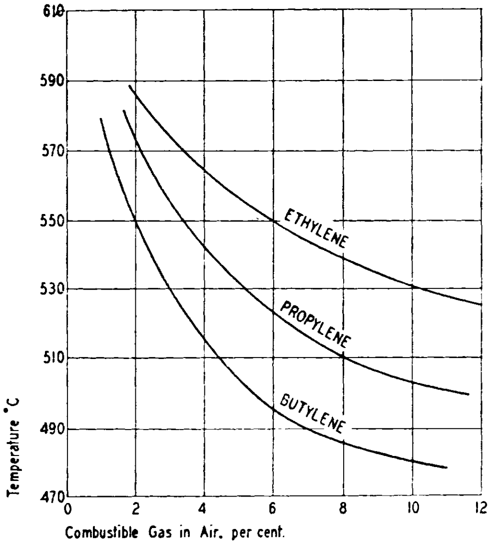
From the curves in Fig. 2, it will be seen that the ignition temperatures decrease as the molecular weight of the hydrocarbon increases, and that the reactions resulting in flame are influenced mainly by the concentration of the combustible gas.

Throughout the temperature range employed in these experiments, the lags on ignition with propylene are longer than those of ethylene or butylene, whilst the lags with ethylene become shorter than those of butylene at 750°. It is suggested that the lower rate of reaction with propylene as compared with ethylene is due to steric hindrance. Ethylene is readily attacked by oxygen, but the presence of the methyl group in propylene hinders the entry of oxygen into the molecule. Propylene thus behaves as the first member of the series, whilst ethylene has certain properties not possessed by the other members, its character being thus in accordance with that of other compounds which are first members of a homologous series.

Mardles (*Trans. Faraday Soc.*, 1931, **27**, 700) has examined the behaviour of ethylene in an engine cylinder, and has also studied its oxidation characteristics (*e.g.*, the temperature coefficient), which he found to be different from those of ethane and at variance, he suggested, with the hypothesis that the first transition during the oxidation of a saturated hydrocarbon is the loss of hydrogen and the formation of the corresponding olefin. From the correlation of the results of his engine experiments and those with a heated tube, Mardles concludes that the phenomena he observed can best be explained by the "peroxidation" theory of combustion. We have proved that ethylene is produced in the pre-flame period during the oxidation of ethane, and that aldehydes are formed during the slow oxidation of both the paraffins and the olefins. Peroxides have not been detected by the use of a 5% solution of titanic sulphate in 5% sulphuric acid. It would seem, therefore, that conclusions as regards pre-flame reactions to be drawn from "heated tube" experiments cannot with certainty be extended to explain the mechanism of combustion in flame.

Lenher (*J. Amer. Chem. Soc.*, 1931, **53**, 3737, 3752), who studied the oxidation of ethylene at temperatures between 360° and 410°, using a flow method and a re-circulation method of experiment, has shown that the reactions are dependent on the experimental conditions to a remarkable degree. He found that formaldehyde was one of the principal intermediate products, whereas Thompson and Hinshelwood (*loc. cit.*, p. 279), who used a static method of experiment at 400—500°, state that "no trace of formaldehyde could be detected by Schryver's test at any stage of the reaction." From our experiments with ethylene and air, which agree closely with those of Lenher with ethylene and oxygen, it would seem that the most important reaction leading to the production of flame is the oxidation of the olefin to an aldehyde.

FIG. 2.



Thompson and Hinshelwood, and Lenher also, have obtained evidence of a chain mechanism in the oxidation of ethylene, but at the comparatively high temperatures employed in our experiments the reactions are not isothermal and accelerate during the lag period until flame appears. The reactions have, therefore, characteristics of thermal reactions.

This work forms part of the researches that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

SAFETY IN MINES RESEARCH STATION,
HARPUR HILL, BUXTON.

[*Received, July 11th,* 1933.]