155. *Oxidation of Ethane, and Cool Flames.*

By J. A. Gray.

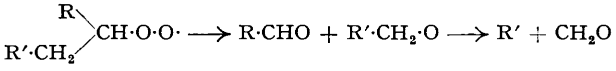
This study has resulted in the formulation of a mechanism for the combustion of ethane which provides an explanation for the intimate connection between oxidation and cracking.

The behaviour of rich ethane–oxygen mixtures has been examined at temperatures above 400°, in a flow system, at atmospheric pressure. Reaction vessels of different sizes and surfaces have been used over a wide range of experimental conditions, including a narrow region—very sensitive to temperature and flow rate—within which the phenomenon of periodic cool flames (not previously reported for ethane) has been observed and investigated.

The gaseous product is rich in ethylene, and at the temperatures used the possibility of a process competing with peroxide and aldehyde formation has been indicated. It is the reaction (*a*) $C_2H_5 + O_2 = C_2H_4 + HO_2$ leading to an autocatalytic build-up of HO_2 to a critical concentration. A fast reaction (*b*) $C_2H_5 + HO_2 = C_2H_4 + H_2O_2$ can then become significant and lead to a rapid increase in $[C_2H_5]$ by $H_2O_2 = 2OH$ and $C_2H_6 + OH = C_2H_5 + H_2O$; (*a*) and (*b*) are competing reactions to which the symbolic equations of Frank and Kamenetzki can be applied to fit a reduced form of the proposed mechanism, giving a periodic dependence on time of $[HO_2]$ and $[C_2H_5]$ to explain the cool flame periodicity.

It is difficult, from previous work, to formulate a reaction mechanism for the oxidation of ethane. Oxidation of hydrocarbons has been reviewed recently by Lewis and von Elbe ("Combustion, Flames, and Explosions of Gases," Academic Press Inc., New York, 1951), Bolland (*Quart. Reviews*, 1949, **3**, 1), and Bawn (*Ann. Reports*, 1950, **47**, 39). Attention has usually been focused on the temperature region (<450°) where the reaction is sufficiently slow to enable rates of pressure change to be measured in a static system. In only one case (Steacie and Plewes, *Proc. Roy. Soc.*, 1934, *A*, **146**, 583) in such a system was ethylene found in the product: this was with a lean (oxygen-rich) mixture at 452° and at an initial pressure well below 1 atm. Present theories of ethane combustion are based principally on the results obtained in this region. The most frequently proposed reaction scheme (Mulcahy, *Discuss. Faraday Soc.*, 1951, **10**, 259) involves intermediate alkyl hydroperoxide and has been verified at low temperatures in the photosensitised oxidation of ethane (Gray, *J.*, 1952, 3150): $R \xrightarrow{O_2} RO_2 \xrightarrow{RH} RO{\cdot}OH + R$, is followed by $-O-O-$ bond fission and subsequent decomposition of the alkoxy-radical to formaldehyde and a smaller alkyl radical. In second-stage ignition, unbranched chains are said to be operative (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 297) by $R{\cdot}CH_2{\cdot}O{\cdot}O{\cdot} \longrightarrow OH + R{\cdot}CHO$, the aldehyde so formed being capable of further decomposition to $RH + CO$.

Lewis and von Elbe, however, consider the bulk of the reaction products to be formed by chains of the type:

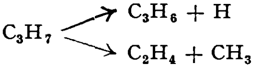


$$\begin{matrix} R \\ R'{\cdot}CH_2 \end{matrix}\!\!>\! CH{\cdot}O{\cdot}O{\cdot} \longrightarrow R{\cdot}CHO + R'{\cdot}CH_2{\cdot}O \longrightarrow R' + CH_2O$$

They consider feasible suggestions for the ethylene-forming reactions; one of them, *viz.*, $C_2H_5 + O_2 = C_2H_4 + HO_2$, is now advanced as an essential part of the reaction scheme. They further visualise the main reaction chain in the oxidation of ethylene as follows:

$$CH_2{:}CH\cdot \xrightarrow{O_2} CH_2{:}CH{\cdot}O{\cdot}O\cdot \xrightarrow{C_2H_4} CH_2{:}CH{\cdot}O{\cdot}OH \longrightarrow 2CH_2O$$

formaldehyde in turn being oxidised. In the oxidation of propane, which was the lowest member of the hydrocarbon series in which cool flames had been observed, they attributed the production of olefins and methane to decomposition of the propyl radical:



$$C_3H_7 \begin{array}{l} \nearrow C_3H_6 + H \\ \searrow C_2H_4 + CH_3 \end{array}$$

There are several recent references to the partial oxidation of ethane (Deanesly and Watkins, *Chem. Eng. Progr.*, 1951, **47**, 134; C.I.O.S. Reports XXVII, 85, item 22; XXXII, 107, item 30; Kooijman, *Rec. Trav. chim.*, 1947, **66**, 5, 205, 491) but no mention has been made of the occurrence of cool flames. Some evidence for the possibility of their existence is provided by Townend and Chamberlain (*Proc. Roy. Soc.*, 1936, *A*, **154**, 95) from explosion-limit curves at pressures greater than atmospheric. At sub-atmospheric pressures similar evidence was obtained by Piazza, Gerstein, and Weast (*Ind. Eng. Chem.*, 1951, **43**, 2721) who upheld the cool-flame hypothesis, but this was not entirely accepted by Delbourgo and Laffitte (*Compt. rend.*, 1951, **233**, 958, 1612).

For methane, neither by direct experiment nor by the study of inflammability limits has there been found any evidence for the existence of cool flames.

EXPERIMENTAL

Cylinder ethane and oxygen (99·8%) (obtained from the British Oxygen Company) were used, except in experiments with purified ethane. The ethane contained: C_2H_6, 94·0; C_2H_4, 3·9; O_2, 0·5; H_2, 0·4; CO, 1·2%; CO_2, nil). The reactants were mixed in a wide-bore tube before entering the reaction vessel at approximately atmospheric pressure, and control was effected by needle-valves and calibrated flowmeters in lines kept at constant pressure by water lutes. The reaction vessel was mounted in a tubular electric furnace, and its temperature was measured by thermocouples strapped to the outside wall. Gas temperatures were measured by a thermocouple in a thin glass pocket which projected into the vessel.

The furnace was kept at a constant given temperature by means of a platinum-resistance thermometer in a bridge circuit, but owing to the sudden onset of exothermic reaction at a critical temperature, independent control of the gas temperature could not be achieved. Total gas-flow rates of 1—25 c.c./sec. were obtainable with tubular reaction vessels of 6, 100, 245, and 363 c.c. of quartz or Pyrex of internal diameters respectively 8, 34, 40, and 47 mm. The composition of the reacting mixture was usually between 55 and 90% of ethane at temperatures from 450° to 800°.

After reaction, the condensable fraction was collected in a cooled receiver at 0° and a sample of the exit gas was drawn off through a side tube, without disturbing the flow-rate, and stored over mercury under slight pressure. The gas was analysed by Gooderham's method (*J. Soc. Chem. Ind.*, 1938, **57**, 388).

In one set of experiments continuous measurement of the infra-red absorption of the exit gases was made on a Grubb–Parsons single-beam instrument, in order to follow the change of ethylene concentration in the exit gas with change of experimental conditions.

The condensable fraction has been examined by a variety of chemical and physical methods; the most useful one for quick determinations was that of polarography, the sample being diluted with N/10-lithium chloride and examined on a "Cambridge" polarograph.

In order to study the effect of surface on the reaction, the following were used: "clean" surfaces, which had been treated with chromic or nitric acid and copious washing with distilled water; potassium chloride surfaces, prepared by rinsing out a clean reaction vessel with concentrated potassium chloride solution, allowing it to drain, and drying it in a current of warm air; surfaces coated with boric acid by rinsing with a 10% solution of boric acid in ethanol, then draining and drying; and surfaces which had been cleaned with 5% hydrogen fluoride and washed with distilled water.

The 245-c.c. reaction vessel had a plane end and was used for detection of the light emission from the cool flames. The exit was then at the side near the plane end, which could be "viewed," after the manner of Ouellet and Ouellet (*Canadian J. Chem.*, 1951, **29**, 76), by a photomultiplier tube, type RCA. 931/A. This was mounted on a cool extension outside the furnace, with its output applied to an oscilloscope, from which a photographic record of the light intensity as a function of time could be obtained.

Observation of Cool Flames in Ethane.—All temperatures quoted are those of the outside wall of the reaction vessel (in °c). The temperature recorded by the thermocouple in the glass sheath in the reaction gas was about 30—50° higher than this when reaction was taking place, and 10° lower when it was not.

FIG. 1. *Cool flame limits for* 70/30 C_2H_6/O_2 *in* 100-*c.c. quartz vessel.*

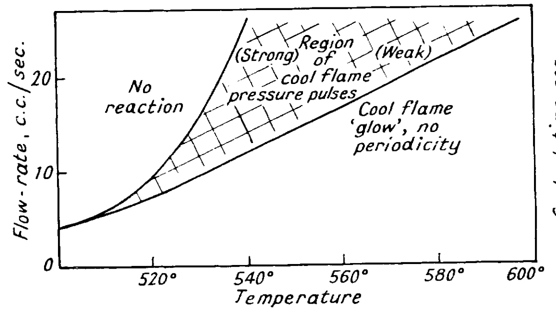
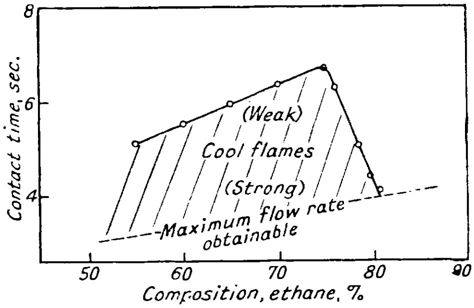


FIG. 2. *Composition–flow-rate limits of observed pressure pulses at* 505°: 238-*c.c. quartz vessel.*



Cool flames were observed in flow systems with reaction vessels not less than 3 cm. in diameter and at relatively fast flow-rates. There was a critical temperature, T_c, below which there was little or no evidence of reaction other than the odour of formaldehyde. At T_c vigorous, spontaneous, cool-flame pressure pulses were observed with a long time interval τ between them. On increase of reaction-vessel temperature the pulses became progressively weaker and more rapid until they could no longer be detected. Increasing the flow-rate had the effect of increasing T_c. A decrease in flow rate narrowed the temperature range over which cool flames were observed, until they were no longer detected (Fig. 1).

FIB. 3. *Dependence of* τ—*the interval between cool flames—on temperature*: 238-*c.c. quartz vessel.*

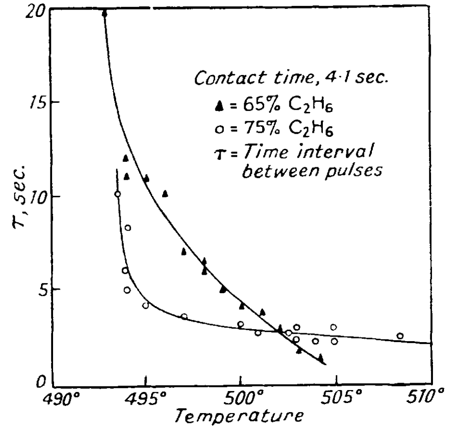
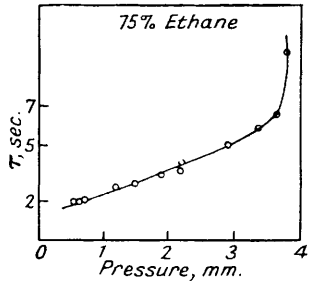


FIG. 4. *Relation between* τ *and the amplitude of the pressure pulse*: 238-*c.c. quartz vessel.*



The effect of the change of mixture composition at a given temperature is shown in Fig. 2, which indicates that a 75/25 ethane/oxygen mixture gave the widest range of flow-rates over which periodic pressure pulses could be obtained. Figs. 3 and 4 show respectively the relationship between τ and reaction temperature, and τ and the amplitude of the pressure pulse. The flames were blue (but could be seen only in the dark) and travelled slowly from the exit to the inlet. Results obtained with the photomultiplier showed that the light intensity during each pulse passed through up to five maxima, the number of which decreased with increasing temperature and weakening of the pressure pulses. This is demonstrated in the oscillograms (all at the same sensitivity) of Fig. 5, which also shows that at the higher temperatures, when pressure pulses were no longer observed, there was a steady background glow. A much weaker glow was detected at temperatures a few degrees below T_c before the cool flames commenced; the intensity of this glow increased with increasing oxygen concentration. Fig. 6 shows the type of reproducibility obtainable under steady conditions of periodic cool flames. Small amounts (up to 7%) of hydrogen or nitrogen had no marked effect but the cool flames were inhibited in mixtures of compositions C_2H_6 45, O_2 15, H_2 40% ; C_2H_6 58, O_2 25, N_2 17%. Fig. 7 shows the repressive effect of a smaller amount of nitrogen on the first one or two peaks. Maximum light intensity was obtained with 50/50 ethane/oxygen mixtures, but results were not obtained for leaner mixtures, for at the temperatures used the cool flames gave rise to " blue " flames which struck back, giving explosive ignition in the cold feed.

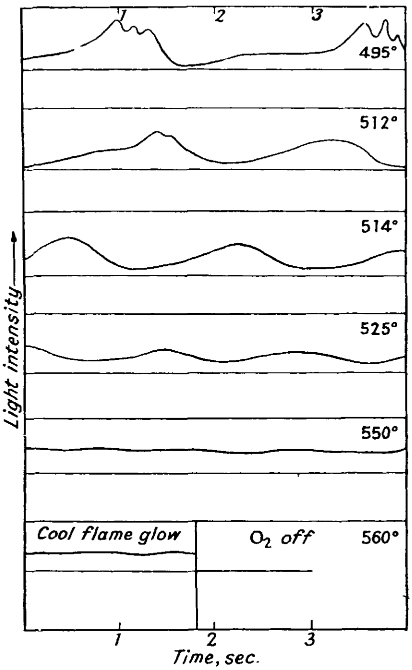


FIG. 5. *Light emission from cool flames in a 75/25 C_2H_6/O_2 mixture ; flow rate,* 17·2 *c.c./sec.,* 245-*c.c. reaction vessel.*

In order to determine whether the cool flames were initiated at a " hot-spot " or were dependent on the bulk temperature of the gas, 60/40 and 70/30 ethane/oxygen mixtures were passed through a 3-cm. diameter tube over a range of flow-rates. The tube was mounted horizontally and was heated by a cylindrical furnace for 20 cm. of its length, and just beyond the furnace the gases passed over an electrically heated platinum spiral. Cool flames could not be induced with a red-hot spiral alone, and pulses were not observed until the furnace temperature had reached that expected for the production of normal cool flames.

FIG. 6. *Light emission from cool flames in a* 75/25 *ethane/oxygen mixture ; flow rate,* 20 *c.c./sec.;* 245-*c.c. reaciton vessel.*

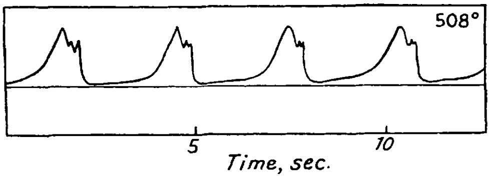
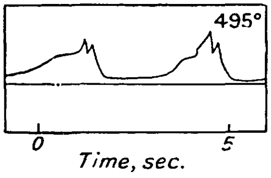


FIG. 7. *Emission from cool flames with added nitrogen.*



In the temperature region immediately below T_c, cool flames could be induced in the normal apparatus by stopping the exit. After an induction period *t*—which decreased with increasing temperature—a single cool flame travelled the length of the tube. After the reaction vessel had been flushed out with fresh feed gas a further pulse could be induced in the same manner.

When t was plotted against temperature, extrapolation of the curve to $t = 0$ gave a temperature very close to T_c. Thus, spontaneous cool flames in the flow system only occurred at temperatures for which the induction period in a static system was very short compared with the interval between the spontaneous pulses.

At low flow rates, or with a small-diameter reaction vessel, no spontaneous or induced cool flames could be detected; but there was a temperature at which rapid reaction set in. For convenience this temperature has also been referred to as T_c. All the experiments quoted above were with ethane from a cylinder, but ethane from which ethylene had been removed by bromination gave similar results, except for a slight tendency to more intense cool flames in the purified gas.

The Non-condensable Products of Oxidation of Ethane.—There was negligible reaction below T_c. Above it, reaction was rapid and 40—80% of the ethane consumed appeared in the product as ethylene. This rapid reaction took place at about 500° in vessels greater than 3 cm. in diameter. Smaller reaction vessels gave no reaction below 600° and no cool flames, but above this temperature reaction was complete, giving a product relatively rich in hydrogen and ethylene. Above T_c over a range of 100° the composition of the products was remarkably insensitive to the temperature of the reaction vessel, suggesting that the temperature of the cool flame and the background glow was constant at about 600° (see Table 1).

TABLE 1.

Initial C_2H_6/O_2	Vessel (vol. in c.c.)	Temp.	Flow rate, c.c./sec.	Composition of exit gas, % *						
				CO_2	C_2H_4	O_2	H_2	CO	C_xH_{2x+2}	CH_4
70/30	363, Pyrex	495°	14·0	1·3	17·2	1·5	5·0	19·7	55·2	—
,,	,,	512	14·0	0·5	16·8	2·0	3·2	16·6	61·0	—
,,	,,	535	14·0	0·3	14·7	2·9	4·3	16·7	61·1	—
,,	,,	540	14·0	1·0	15·7	1·0	3·0	18·1	61·4	—
,,	,,	523	30·1	0·9	22·8	0·5	9·7	16·9	49·1	—
									C_2H_6	
,,	245, Quartz	617	5·0	1·6	23·9	0·4	15·8	19·2	27·4	11·8
60/40	100, Quartz Clean	525	7·1	3·6	16·8	7·7	10·0	27·0	23·7	11·2
60/40	Coated B_2O_3	560	7·1	4·8	16·7	5·9	8·8	29·6	24·2	9·9
70/30	,,	520	16·7	0·9	11·5	9·0	2·0	8·3	65·5	2·7
70/30	,,	540	16·7	0·9	11·1	8·5	2·0	8·0	68·1	1·3
70/30	6, Quartz coated B_2O_3	610	3·0	1·2	29·1	0·5	21·4	18·6	22·0	7·0
70/30	,,	700	3·0	1·0	31·1	0·3	22·5	19·4	17·3	8·5

* Analysis figures accurate to ±0·5%.

The flow-rate had to exceed a critical value in order to produce cool-flame pulses (Fig. 1). Below it, the nature of the products was not substantially altered but the effect of increasing the flow-rate again was to decrease the amount of recombination of ethylene and hydrogen. Further increase in the flow-rate resulted in the incomplete reaction of oxygen.

A surface treated with hydrogen fluoride completely inhibited cool-flame pulses. Stainless-steel favoured carbon dioxide formation, but boric acid, potassium chloride, quartz, and Pyrex surfaces were all very similar in their effect. The limits of exit gas composition (for which analyses are available) formed with different reaction vessels for 70/30 mixtures are summarised in Table 2.

TABLE 2. *Analysis*, %.

Vessel	CO_2	C_2H_4	O_2	H_2	CO	C_2H_6	CH_4
6 C.c., Quartz, clean or B_2O_3-coated	0—3	25—33	0—1	9—23	16—23	8—25	6—10
KCl-coated	0—3	25—33	0—1	19—31	14—20	8—25	6—10
100 C.c., quartz	1—5	10—24	1—17	2—20	8—30	10—35	4—13
245 C.c., quartz	1—2	9—24	0—6	3—6	14—19	40—50	6—9
363 C.c., Pyrex	0—3	15—26	0—5	3—10	13—24	—	—
400 C.c., stainless steel	2—9	9—20	0—17	1—8	3—15	37—67	3—10

Podbielniak distillation confirmed that the unsaturated hydrocarbon was ethylene. The only other olefin present was the trace of propylene which had been shown to be present in the original (liquid) ethane by analysis with a mass-spectrograph.

Addition of hydrogen increased the extent of hydrogenation of ethylene. The results in Table 3 are from the usual 70/30 mixture diluted with 20% of nitrogen or hydrogen; they have been corrected for excess of diluent additive for comparison.

The hydrogenation reaction, as shown by the effect on the ethylene : carbon monoxide ratio, is favoured by added hydrogen but hindered by nitrogen.

The increased methane in the third run shown in Table 3 is probably due merely to an increase in ethane decomposed. The difficulty in such comparative experiments, where an attempt is made to study the effect of a single variable, is that strictly comparable conditions are rarely obtainable. The main variables are temperature, flow-rate, composition, nature of surface, vessel length and diameter, conversion, and additives. The aim has been to make comparisons (where possible) at constant conversion—the fraction of the original ethane decomposed—or to compare conversions while varying a single factor. The relationship between methane and conversion mentioned above is brought out in Fig. 9, which demonstrates that methane is formed progressively during the reaction and that it is being consumed more slowly than ethane. This result is not surprising but it is reassuring to find that some correlation can be obtained from a large number of gas analyses over such a wide range of conditions: these varied from 43 to 30% of O_2; 500° to 700°; contact times of 0·15 to 10 seconds in vessels of volume 6 to 400 c.c.; with surfaces of quartz, Pyrex, boric acid, potassium chloride, stainless-steel, and, in one case only, a surface treated with hydrogen fluoride.

TABLE 3. (245-C.c. plane-ended reaction vessel at 570°, and 20 c.c./sec.).

	Composition of products, %						
Additive	CO_2	C_2H_4	O_2	H_2	CO	C_2H_6	CH_4
Nil	1·7	17·2	4·1	5·3	18·0	46·2	8·1
N_2	1·4	19·5	4·6	4·2	14·6	48·3	7·2
H_2	1·9	13·1	5·7	6·3	19·4	43·6	10·2

FIG. 8. *Relation between* t *(the induction period between stoppage of the exit and the appearance of a single, induced cool flame) and temperature ;* T_c *is the temperature at which spontaneous cool flames commenced in the flow system :* 100-*c.c. quartz vessel.*

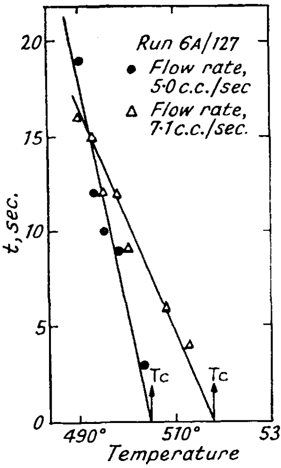
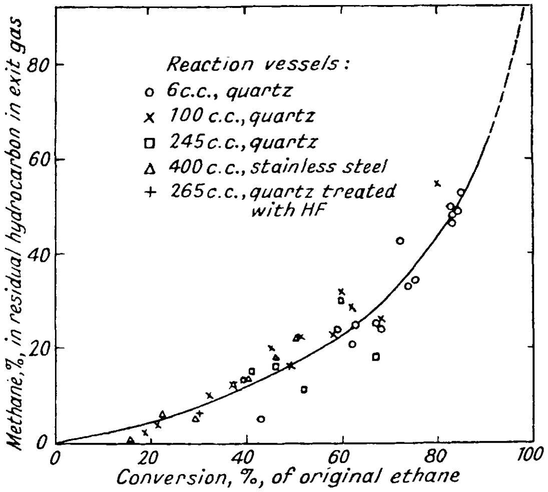


FIG. 9. *Relationship between the % of conversion and the % of methane in the unburnt hydrocarbon ; varying flow-rate, temperature, and vessel diameter for* 70/30 *and* 60/40 C_2H_6/O_2 *mixtures.*



The nature of the products was very similar whether vigorous cool flames were evident or whether the sample was taken at a higher temperature, where only a weak background glow could be detected with the photomultiplier. The following analyses (%) referring to 70/30 mixtures and the 245-c.c. reaction vessel are typical :

Temp.	Flow rate, c.c./sec.	CO_2	C_2H_4	O_2	H_2	CO	C_2H_6	CH_4	
513°	15·9	1·4	14·8	4·9	4·4	16·3	51·8	6·4	Pulsing
532	20·0	2·2	17·9	5·0	3·7	14·2	47·8	9·1	Pulsing
560	20·0	1·2	16·9	4·6	5·4	16·0	46·9	9·0	No pulses
570	15·9	1·7	17·2	4·1	5·3	18·0	46·3	8·0	No pulses

Trial experiments with no oxygen showed that thermal decomposition of ethane became of importance only above 650° for the larger vessels (and 750° for the 6-c.c. reaction vessel). The production of ethylene with the sudden onset of cool flames is shown in Fig. 10, which is a continuous record of the infra-red absorption at 950 cm.$^{-1}$ of the exit gas.

A similar result was obtained with a 60/40 mixture on occasions when the cool flame pulses were preceded by violent ignition accompanied by a blue or a yellow flame. The same amount of ethylene was formed whether by cool flame or by true ignition.

In general, at fast flow-rates, the quantity of ethylene in the product always exceeded that of carbon monoxide, which in turn was considerably greater than that of hydrogen except in the 6-c.c. vessel in which hydrogen exceeded carbon monoxide but was always less than ethylene. The nature of the surface had no marked effect on the products except for stainless steel, which is known to favour the formation of carbon dioxide. Potassium chloride necessitated a higher temperature for initiation of the reaction, but boric acid had little effect. Cool flames in 70/30 mixtures were completely inhibited in a 265-c.c. quartz reaction vessel (internal diameter 40 mm.) which had been treated with 5% hydrogen fluoride; after the vessel had been once re-fired, cool flames were again induced. Product analyses were as follows :

FIG. 10. *Production of ethylene with the onset of cool flames in* 60/40 C_2H_6/O_2 : 238-*c.c. quartz vessel; flow-rate,* 20 *c.c./sec.*

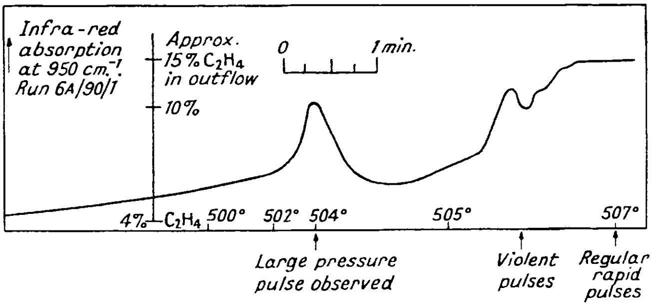


FIG. 11. *Variation of product composition with composition of feed gas :* 363-*c.c. Pyrex reaction vessel;* 515°.

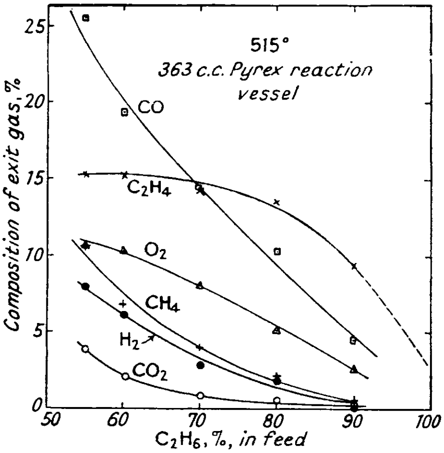
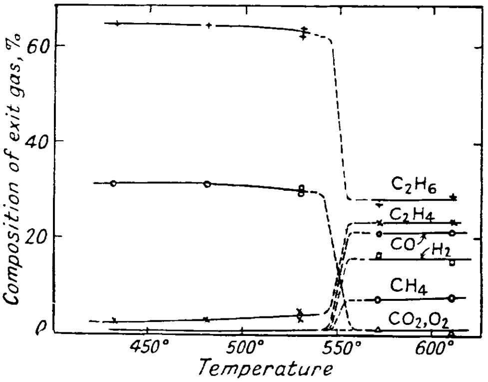


FIG. 12. *Composition of exit gas from a* 70/30 C_2H_6/O_2 *mixture :* 6-*c.c. quartz reaction vessel; flow-rate* 1 *c.c./sec.*



Temp.	CO_2	C_2H_4	O_2	H_2	CO	C_2H_6	CH_4	
500°	1·7	14·3	9·9	2·7	13·0	54·8	3·5	HF-treated, no pulses
461	0·5	12·2	18·7	5·4	10·8	52·4	nil	Reactor re-fired, pulsing

The lowest reaction-vessel temperature at which spontaneous cool flames had been observed was 461°, although induced pulses have been obtained at 430°.

Increase of the oxygen between the limits 10—45% seemed to affect only the amount of ethane consumed, the products all increasing steadily in approximately constant ratios—apart from ethylene which began to decrease presumably owing to oxidation, in the leaner mixtures. The results are shown in Fig. 11 for the 363-c.c. Pyrex vessel; similar results were obtained with a 100-c.c. quartz vessel.

It was not possible to make comparisons of gas analysis results very close to T_c. Once cool flames had started, independent control of the temperature of the reaction vessel was lost and that of its wall rose. By use of large vessels and a suitable flow-rate it was possible to limit the consumption of oxygen so that quantities up to 10% or more occurred in the exit gas. This could not be done in the 6-c.c. vessel, for which results above and below T_c are given in Fig. 12; intermediate results could be obtained only when the feed was diluted with nitrogen, but cool flame pressure pulses could not be obtained under any conditions.

Ethylene was also the most important gaseous product to be formed in the induction period preceding explosion in an oxygen-rich mixture. A 30/70 C_2H_6/O_2 mixture was passed through the 6-c.c. reaction vessel, through a condenser, and then through a gas-sampling tube which had a tap at each end. On slow increase of the reaction-vessel temperature an explosion took place at 595° which destroyed the feed line and interrupted the flow. Closure of the two taps on the sampling tube isolated a sample of gas which had passed through the reaction vessel just below the explosion temperature. The analysis of this sample is compared below with that of a sample taken at a lower temperature (545°) before any appreciable reaction had taken place.

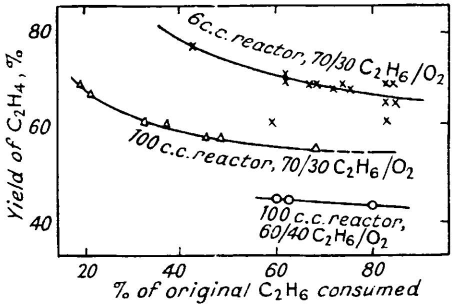


FIG. 13. *Dependence of the yield of ethylene on ethane conversion.*

Flow rate, 1 *c.c./sec.*

	CO_2	C_2H_4	O_2	H_2	CO	C_xH_{2x+2}
Initial composition, %	Nil	1·9	64·3	Nil	1·1	32·9
Pre-explosion composition, %	0·4	5·0	62·4	Nil	1·6	30·4

The consumption of oxygen with the almost exclusive formation of ethylene indicates that the reaction in progress in the pre-explosion temperature region is not merely thermal cracking of ethane.

It will be seen from Fig. 13 that yields of ethylene plotted against conversion lie on separate curves for different diameters and reactant compositions.

The Condensable Product.—This was collected in an ice-cooled receiver, and occasionally in a trap at −80°. It consisted of a dilute aqueous solution of formaldehyde, acetaldehyde, acids, and peroxides. The main interest was in the nature of the peroxide, for which polarographic examination of the condensate gave no conclusive results. A polarogram of a product diluted to 1/400 with N/10-lithium chloride gave a distinct early step, starting at 0·3 v, which flattened off at 0·8 v, and then continued to increase in the manner usually associated with hydrogen peroxide or hydroxyalkyl peroxides. The polarographic waves due to formaldehyde (1·72 v) and acetaldehyde (1·98 v) were clearly seen. The separation of the peroxidic wave into two distinct portions could be achieved only at the optimum conditions of dilution and sensitivity (in this case 1/70), but in no case could such a resolution be achieved with synthetic mixtures of ethyl hydroperoxide and hydrogen peroxide with or without the addition of formaldehyde. This (purely negative) evidence did suggest that some other peroxidic species might be present, possibly by condensation of hydrogen peroxide with another reaction product. In all other respects the condensable product was similar to that obtained by earlier investigators.

DISCUSSION

From the manner in which the reaction rate depends on vessel diameter it is probable that chain initiation occurs in the volume of the gas and chain destruction at the wall. The main points that emerge from the gas-analysis results have already been indicated. The examination of the condensable product has not revealed anything new, other than casting doubt on the identity of the peroxide. The occurrence of cool flames—previously unsuspected—is interesting, but little can be learnt yet from the oscillograms other than that visible light is emitted. It is assumed that the emitter is excited formaldehyde and that the cool flames are conventional in this respect. Confirmation that the observed flames are true cool flames comes from B. P. Mullins (private communication and National Gas Turbine Establishment Report No. R.96) who has noted cool flame phenomena in ethane/air mixtures between 600° and 800° while making ignition-delay measurements in a continuous flow turbine rig. The observation most difficult to reconcile with generally accepted theories of ethane oxidation is the production of ethylene in up to 80% yield. Although the results do not point unambiguously to the scheme given below, it is plausible that the presence of a free valency in the form of an ethyl radical from an unspecified initiating reaction should result in the following reaction cycle to yield ethylene :

$$(1)\ C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2$$
$$(2)\ HO_2 \xrightarrow{\text{wall}} \text{Inert product}$$

By attack on ethane this scheme can lead to an autocatalytic build-up of HO_2 :

$$(3)\ HO_2 + C_2H_6 \longrightarrow H_2O_2 + C_2H_5$$
$$(4)\ H_2O_2 \longrightarrow HO + OH$$
$$(5)\ OH + C_2H_6 \longrightarrow H_2O + C_2H_5 \text{ followed by (1)}$$

This sequence of reactions is not unlike that occurring in the hydrogen–oxygen reaction at the third explosion limit, where HO_2 radicals are present in the gas phase in quantity sufficient to react with hydrogen by $HO_2 + H_2 \longrightarrow H_2O_2 + H$. If the reaction

$$(6)\ C_2H_5 + HO_2 \longrightarrow C_2H_4 + H_2O_2$$

which may be supposed to be rapid, is now introduced (followed again by decomposition of H_2O_2) the possibility arises of reducing the reaction scheme to an approximation of the Frank–Kamenetzki equations (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 671) :

$$\left.\begin{array}{l} A + X \longrightarrow B + 2X \\ X + Y \longrightarrow B + 2Y \\ A + Y \longrightarrow B \end{array}\right\} \begin{array}{l}\text{where A is the reactant, B represents inert} \\ \text{products, } X = HO_2\text{, and } Y = C_2H_5\end{array}$$

This leads to the two equations :

$$(a)\ dx/dt = k_1ax - k_2xy \qquad (b)\ dy/dt = k_2xy - k_3ay$$

and a periodic solution for [X] and [Y]. This scheme has been examined and developed by Walsh (*Trans. Faraday Soc.*, 1947, **43**, 305), Denbigh, Hicks, and Page (*ibid.*, 1948, **44**, 479), and Moore (*ibid.*, 1949, **45**, 1098). It is symbolic only, as each of the reactions involves a number of processes, but the periodic form of the solution for $[HO_2]$ and $[C_2H_5]$ does suggest that the cool-flame periodicity may be inherent in the reaction mechanism and does not necessarily depend on localised heating and cooling effects of the system.

When decomposition of HO_2 occurs to give relatively inert products, it may be expected that the reaction

$$(7)\ C_2H_5 \longrightarrow C_2H_4 + H$$

becomes important and that the H_2 formed, particularly in the smallest reaction vessel, is a result of

$$(8)\ H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

In the larger vessels equation (7) may set the upper limit to the cool-flame temperature. Any tendency for self-heating in the reacting mixture results in the increased importance of equation (7) and the interruption of reaction chains with a decrease in the overall rate of reaction.

The mechanism given above may compete with the conventional peroxide scheme or, above T_c, may be more important. Subsequent oxidation of ethylene as an intermediate can account for secondary products—including methane, which is formed in significant amount in the oxidation of ethylene alone. In the ethane system it may be formed either by $C_2H_5O \longrightarrow HCHO + CH_3 \xrightarrow{C_2H_6} CH_4 + C_2H_5$ or, if the peroxide mechanism is excluded, by

$$(9)\ H + C_2H_6 \longrightarrow CH_4 + CH_3$$

The reaction of hydrogen atoms with oxygen—requiring a ternary collision—may well be slow compared with (9). The latter equation is supported by the evidence, summarised by Steacie (" Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, 1946), for the production of methane on mixing hydrogen atoms and ethane.

Hydrogen peroxide as an essential intermediate receives support from Kooijman's finding (*loc. cit.*) that with ethane and propane the principal peroxide found in the condensate was hydrogen peroxide. This is not in disagreement with previous evidence (cf. Harris, *Discuss. Faraday Soc.*, 1951, **10**, 318, who emphasises that organic peroxides as such were only invoked in the initiation of the reaction). A further complication in elucidating the processes by which the products arise is that in experiments with ethylene/oxygen mixtures ethylene was oxidised at lower temperatures than ethane (in large-diameter vessels) and that in the 6-c.c. vessel the reverse was true. For instance, in the 363-c.c. Pyrex vessel, spontaneous yellow flames appeared at 430°, suggesting that the final gaseous products of ethane oxidation (CO, CO_2, H_2O, CH_4) are, in part, derived from ethylene. As in the case of ethane, no flames were observed in the 6-c.c. vessel. These relative rates of oxidation may account for the high yields of ethylene in the 6-c.c. vessel, and the lower yields in the 100-c.c. vessel (Fig. 13).

Postulation of HO_2 as the chain carrier derives indirect support from the work of Walsh and his collaborators (" 3rd Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins Co., Baltimore, 1949, 389; *J. Roy. Inst. Chem.*, 1951, **75**, 323) who identify the active anti-knock agent from tetraethyl-lead as lead oxide and suggest HO_2 as one of the likely chain carriers being destroyed.

The reaction scheme requires that HO_2 should be able to build up to a critical concentration before rapid reaction sets in. When this critical concentration is reached, at T_c, reaction (6) becomes significant and dy/dt in equation (*b*) becomes positive. HO_2 has been regarded as an intermediate of comparatively long life (Minkoff, *Discuss. Faraday Soc.*, 1947, **2**, 151) so that it is able to diffuse to the wall and become a vehicle for the destruction of free valencies. In the hydrogen–oxygen reaction under comparable conditions, its life-time has been estimated by Lewis and von Elbe (*op. cit.*) to be of the order of 1 second. It is thus to be expected that there will exist, in this type of reaction, a critical vessel diameter above which chain-branching reactions are more important than the chain-breaking wall reactions. The presence of olefins in significant amount in the products of oxidation of hydrocarbons higher than ethane (for a recent summary see Garner and Petty, *Trans. Faraday Soc.*, 1951, **47**, 884) and even ether (McCormac and Townend, *J.*, 1940, 151) suggests that the reaction $R + O_2 \longrightarrow$ olefin $+ HO_2$ may be of more general application in explaining how an apparently thermal decomposition can take place alongside direct oxidation, although under otherwise identical conditions no decomposition takes place in the absence of oxygen. The reaction of an alkyl radical with oxygen may be expected to have a much lower activation energy than that of a decomposition such as $R{\cdot}CH_2{\cdot}CH_2{\cdot} \longrightarrow R{\cdot} + C_2H_4{\cdot}$. The latter reaction can account satisfactorily for the final production of methane and ethylene (if R = Me), but in the oxidation of ethane the intervention of such a " cracking " chain initiated by $C_3H_8 + OH \longrightarrow H_2O + C_3H_7$ depends on the accumulation of C_3H_8 as an intermediate; this is a process which would appear to be inconsistent with the reactivity of hydrocarbon radicals in the presence of oxygen.

No mention has been made of the processes by which methyl radicals are removed (other than by hydrogen-abstraction to give methane) as they are not essential to the main argument, but it has been found (Gray, *op. cit.*) that with oxygen, at temperatures up to 70° and possibly up to at least 400°, only the reactions $CH_3 + O_2 \longrightarrow CH_3{\cdot}O{\cdot}O{\cdot} \longrightarrow CH_3{\cdot}O{\cdot}OH$ are of importance.

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