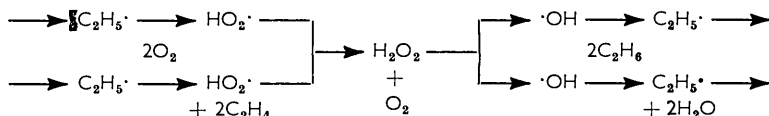**976.** *The Reaction Between Ethane and Oxygen at* 600—630°.

By R. J. Sampson.

The reaction at 600—630° between ethane and oxygen in a flow-reactor with a reaction time of a few hundreths of a second gives rise, at small conversions, mostly to ethylene and water, together with hydrogen, hydrogen peroxide, formaldehyde, methane, carbon monoxide, acetaldehyde, ethylene oxide, methanol, butane, ethanol, and propane (the yields decreasing in that order). The reaction rate, and the influence of variables on it, are semi-quantitatively explained in terms of a quasi-stationary-chain mechanism involving hydrogen peroxide as a carrier of two active centres:
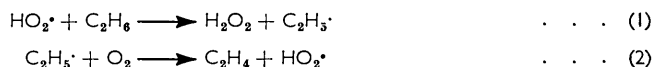
$$\longrightarrow \; C_2H_5 \cdot \longrightarrow HO_2 \cdot \longrightarrow \atop \longrightarrow \; C_2H_5 \cdot \longrightarrow HO_2 \cdot \longrightarrow \quad \Big] \longrightarrow \; {H_2O_2 \atop + \atop O_2} \longrightarrow \; \Big[{\cdot OH \longrightarrow C_2H_5 \cdot \longrightarrow \atop \cdot OH \longrightarrow C_2H_5 \cdot \longrightarrow}$$

with $2O_2$ and $+ 2C_2H_4$ on the left branch, $2C_2H_6$ and $+ 2H_2O$ on the right branch.

The results are consistent with formation of the majority of most minor products through the ethoxy-radical:

$$C_2H_5 \cdot + HO_2 \cdot \longrightarrow [C_2H_5 \cdot O \cdot OH] \longrightarrow C_2H_5 \cdot O \cdot + \cdot OH$$
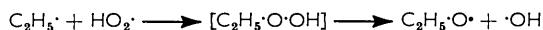
Evidence is given concerning the origin of the remaining products.

The mechanisms of oxidation of hydrocarbons at temperatures above those at which the negative temperature coefficient operates have been studied in this laboratory for some time. This paper deals with the reaction of ethane at 600—630°, at a total pressure of 1·1 atm. and at ethane–oxygen ratios between 2·5 and 10.

It has frequently been suggested [1-3] that the chain mechanism which operates in oxidation of paraffins involves attack of $HO_2 \cdot$ on the paraffin, *e.g.*, reactions (1) and (2), at least in the early stages before the concentration of primary products has become large enough for attack on them to become appreciable:

$$HO_2 \cdot + C_2H_6 \longrightarrow H_2O_2 + C_2H_5 \cdot \qquad \cdot \;\; \cdot \;\; \cdot \;\; (1)$$

$$C_2H_5 \cdot + O_2 \longrightarrow C_2H_4 + HO_2 \cdot \qquad \cdot \;\; \cdot \;\; \cdot \;\; (2)$$

The amounts of hydrogen peroxide isolated have invariably been considerably lower than those which should be formed if reactions (1) and (2) represent the main chain-carrying steps; the small yields have been attributed to decomposition of hydrogen peroxide (especially on the walls) rather than to its non-formation. Only in the low-temperature oxidation of alcohols [4] have the products supported a mechanism analogous to (1) and (2).

Knox and Trotman-Dickenson [3b-d] and their co-worker have suggested that the hydroperoxide chain applies in oxidation of paraffins at temperatures as low as 318°. On the other hand, their work on competitive oxidations [3c,5] showed that the radical which attacks the paraffin displays (like $\cdot OH$) little discrimination between C–H bonds of varying strength. Significant differences in the activation energies would, however, be expected if the attacking radical is $HO_2 \cdot$: step (1) is about 7 kcal. mole^{-1} endothermic and the analogous step for

[1] J. A. Gray, *J.*, 1953, 741.
[2] (a) Satterfield and Wilson, *Ind. Eng. Chem.*, 1954, **46**, 1001; (b) Satterfield and Reid in " Fifth Symposium (International) on Combustion," Reinhold Publ. Corp., New York, 1954, 511.
[3] (a) J. W. Falconer and J. H. Knox, *Proc. Roy. Soc.*, 1959, *A*, **250**, 493; (b) J. H. Knox, *Trans. Faraday Soc.*, 1959, **55**, 1362; (c) J. H. Knox, Smith, and Trotman-Dickenson, *ibid.*, 1958, **54**, 1509; (d) J. H. Knox, *ibid.*, 1960, **56**, 1225; (e) W. E. Falconer, J. H. Knox, and Trotman-Dickenson, *J.*, 1961, 782.
[4] (a) A. R. Burgess, Cullis, and Newitt, *J.*, 1961, 1884; (b) A. R. Burgess and Cullis, *J.*, 1961, 3041.
[5] W. E. Falconer, J. H. Knox, and Trotman-Dickenson, *J.*, 1961, 782, 4285.

some of the other paraffins which were oxidised in competition should be nearly thermo-neutral.*

In the present work, product distribution and kinetic criteria have been used to throw light on the mechanism of oxidation of ethane at about 600°. It is shown that the results are explicable if $HO_2\cdot$ attack on the paraffin does not occur as a predominant chain-step: the main attack is by hydroxyl radicals.

<div align="center">EXPERIMENTAL</div>

Apparatus, Procedure, and Analyses.—A simplified diagram of the oxidation apparatus is given in Fig. 1. A flow-system was used, including a unit of fused silica combining two preheaters (for preheating separately air and ethane), a mixing device, a reactor, and a quenching device.
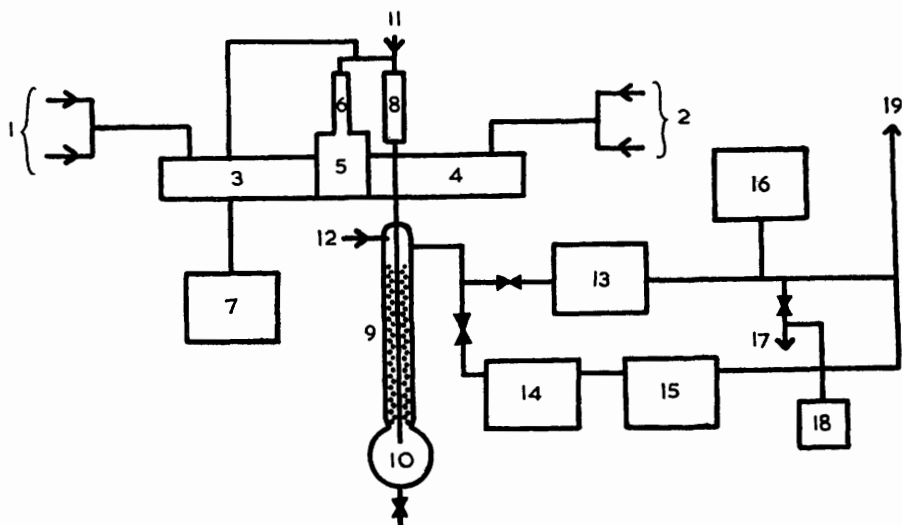

<div align="center">FIG. 1. General lay-out of oxidation apparatus.</div>

1, From N_2 and C_2H_6 metering and controlling devices.
2, From N_2 and air metering and controlling devices.
3, Ethane preheater.
4, Air preheater.
5, Reactor.
6, Quenching capillary.
7, Gas chromatograph for acetaldehyde, etc., and for butane, etc.
8, Water-cooled condenser.
9, Moist beads for scrubbing gas.
10, Liquid collection vessel.
11, From water reservoir (for washing 8 before and after a run).
12, From water reservoir (for washing 9 before and after a run).
13, Gas-meter for main-stream.
14, Bubbles for final scrubbing (side-stream).
15, Gas-meter for side-stream.
16, Gas chromatograph for ethylene, etc.
17, Sampling point for g.l.c. samples.
18, Pump for evacuation of g.l.c. sample tube.
19, To stack.

The preheaters [length 1 m., internal diameter (i.d.) 2·0 cm.], packed with silica chips, were wound directly with " Brightray " heating wire and were thoroughly lagged. Each was fitted with an axial pocket for a movable thermocouple. The preheated gases were mixed by bringing them together in a capillary [situated within the reactor (Fig. 2)] of i.d. 2·0 mm. and length

* The HO_2–H bond strength is ~90 kcal.; [6] the C_2H_5–H bond strength is ~97 kcal.,[7] whereas some of the C–H bond strengths of other paraffins which were oxidised in competition are considerably lower.

[6] Foner and Hudson, *J. Chem. Phys.*, 1962, **36**, 2681.
[7] B. E. Knox and Palmer, *Chem. Rev.*, 1961, **61**, 247.

1·6 cm. The flow within this capillary was well within the turbulent régime, thus ensuring rapid, thorough mixing. The time in the mixing capillary was less than 1% of the time in the reactor, whose volume was 18 ml. On leaving the capillary, the gases entered the reaction chamber flowing in the direction opposite to that of the general flow in this chamber; in this way stagnant gas pockets, commonly met in small flow reactors,[8] were reduced. The nature of the flow within the reactor would not have been fully turbulent; on the other hand, the length : diameter ratio was not great enough for pure streamline flow to have become established. The only heat-input to the reactor, which was well lagged, was that provided by the reactants. The reactor was fitted with an axial pocket for two movable thermocouples. The reaction mixture within the reactor was not strictly isothermal; however, temperature variations were relatively small. Thus, when the average temperature measured with the reactor thermocouples was 623°, the variation from point to point was within 5° of this value. The gases left the reactor by another capillary (i.d. 2·2 mm., length 25 cm.), in which the turbulent gas flow caused rapid heat-transfer to this capillary's water-cooled walls. During the passage of the gas through this quenching capillary, the gas temperature fell about 500°, e.g., from 623° to 110°. Since the capillary volume was only 5% of the reactor volume, the reaction was sharply arrested.

Fig. 2. Oxidation reactor.
1, Reactor space.
2, Ethane preheater.
3, Air preheater.
4, Mixing capillary.
5, Quenching capillary.
6, Water jacket.
7, Thermocouple pocket.
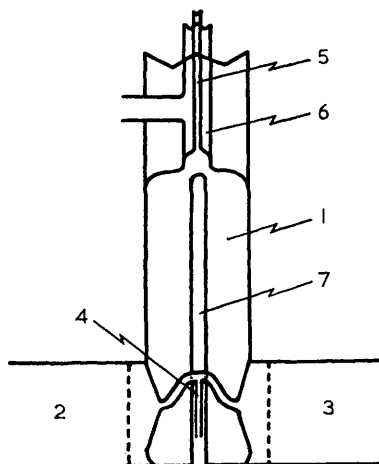
To find whether there was any decomposition of hydrogen peroxide in the quenching capillary a special apparatus with a quenching capillary and collecting system, like those used in the oxidation apparatus, was employed. In a series of experiments under simulated reaction conditions, with either air or ethane to simulate the hot reaction gases, between 76% and 94% (average 88%) of the hydrogen peroxide entering the capillary was recovered. In the oxidation experiments it was accordingly assumed that recovered hydrogen peroxide represented 88% of that entering the capillary.

Ethane and nitrogen (each at 250 l./hr.) were metered (by rotameters) to the preheaters; then the nitrogen was stepwise replaced by air. After a time sufficient for the reactor temperatures to become stabilised, the hydrogen peroxide-collection system (a water-cooled condenser followed by a bed of glass-beads) was thoroughly washed with water. After a further period of steady running, during which gas analyses were made (see below), the collection system was washed again. The hydrogen peroxide content of the washings was determined iodometrically. Formaldehyde, together with any formic acid in the washings, was determined by treating another portion with silver oxide [9] (which oxidises the formaldehyde to formic acid) and then determining the total formic acid by mercuric chloride.[10] A small proportion of the formaldehyde remained in the gas after passage through the wet beads; this was determined by bubbling a metered side-stream through water whose formaldehyde content was subsequently determined.

[8] Batten, *Austral. J. Appl. Sci.*, 1961, **12**, 11.
[9] Bailey and J. H. Knox, *J.*, 1951, 2741.
[10] Berl, " Berl-Lunge, Chemisch-technische Untersuchungsmethoden," Springer, Berlin, 1932.

Acetaldehyde, ethylene oxide, methanol, and ethanol were measured by taking a stream (5 l./hr.) of gas immediately after the quenching by way of a glass-tube (at 95°) directly through the sampling valve of a gas chromatograph (dinonyl phthalate capillary column at 0°; flame ionisation detector). C_3 and C_4 hydrocarbons were determined by similarly taking a stream to a gas-chromatography column at 0°, packed with tetraisobutene on " Celite." Ethylene was determined by passing a stream of the product gas, taken after passage through the wet glass beads, to a similar tetraisobutene column. Methane, hydrogen, and carbon oxides were de-termined by gas chromatography of samples of the exit-gas taken by opening an evacuated tube to the exit-gas line.

The influence of oxygen partial pressure was investigated by replacing the stream to the air preheater by (air + nitrogen) or (air + oxygen), while keeping the total flow constant at 250 l./hr. In this way runs were carried out in which the oxygen pressure was approximately halved, and approximately doubled, relative to its value in the runs with air only. The ethylene content of the exit gas in these runs was monitored by measuring the intensity of infrared absorption by ethylene at 10·55 μ with a Grubb-Parsons DMI spectrometer as a continuous analyser. This method gave satisfactory comparative results, but the chromatographic method was generally preferred. In these runs analyses for products other than ethylene were not made.

Ethylene, when required in the feed, was metered into the ethane stream, which was corre-spondingly reduced. When acetaldehyde was required as an additive it was fed as a liquid to the ethane preheater by a micro-pump. When required, hydrogen bromide and chlorine were metered to the air-preheater; bromine was included in the air-feed by passing a metered fraction of the latter through saturated bromine water at 0°.

Materials.—Ethane was normally Matheson's Chemically Pure grade. It contained less than 0·5% of ethylene and about 0·1% of propene. Separate experiments showed that additional quantities of these impurities had no detectable influence on the results (except as indicated in the Results section). In the experiments on variation of oxygen partial pressure, BOG ethane was used; it contained about 3% of ethylene.

Ethylene was Imperial Chemical Industries Limited's polymer-grade material. Chlorine was from the same firm. Bromine was " AnalaR " grade. Hydrogen bromide was Matheson's Chemically Pure grade. Acetaldehyde was from Distiller's Co., Ltd. (>98% pure). Air was a piped laboratory supply of filtered, dried, and carbon dioxide-freed gas.

RESULTS

Fig. 3 shows the conversion of ethane into ethylene as a function of temperature for equal volumes of ethane and air and a reaction time of 47 msec. Fig. 4 shows the hydrogen peroxide yield as a function of ethylene yield for the same conditions. In the absence of oxygen,

TABLE 1.

Products from ethane oxidation at 623° (2·0% conversion of ethane into ethylene).

(Yields in moles formed per 100 moles of ethylene formed.)

Product	Yield	Product	Yield	Product	Yield
C_2H_4	100	CH_4	6·0 ± 1	MeOH	0·40 ± 0·15
H_2O	Not determined	CO	3·5 ± 1	n-C_4H_{10}............	0·25 ± 0·05
H_2O_2	9·5 ± 1 †	Me·CHO	1·5 ± 0·4	EtOH	0·15 ± 0·07
H_2	10·5 ± 1·5	$(CH_2)_2O$	1·0 ± 0·4	C_3H_8	0·10 ± 0·05
CH_2O *	8·0 ± 1				

* Strictly formaldehyde + formic acid; the chromotropic acid test showed that if formic acid was present, its proportion, relative to formaldehyde, was small. † Corrected for decomposition in the capillary.

thermal cracking of ethane was negligible. Table 1 shows the yields of minor products relative to ethylene. It is unlikely that any product formed in yield comparable with the smallest yield listed escaped detection. A trace of propene may have been formed; if so, it was small compared with the propene present in the ethane, which precluded the estimation of any formed as a product. No C_4 hydrocarbon other than n-butane was detected. Carbon dioxide was not detected. A trace of acetylene may have been formed.

Table 2 shows the yields of certain products as a function of conversion. To investigate the

TABLE 2.

Variation of yields with conversion.

Temp.	Conversion (%), $C_2H_6 \longrightarrow C_2H_4$	Moles of product per 100 moles of C_2H_4 formed			
		H_2O_2 *	CH_2O	CH_4	CO
613°	1·0	13·5 ± 1	7·5 ± 1	4·0 ± 1	2·0 ± 0·5
623	2·0	9·5 ± 1	8·0 ± 1	6·0 ± 1	3·5 ± 1
632	3·0	7·1 ± 1	8·5 ± 1	6·0 ± 1	4·3 ± 1

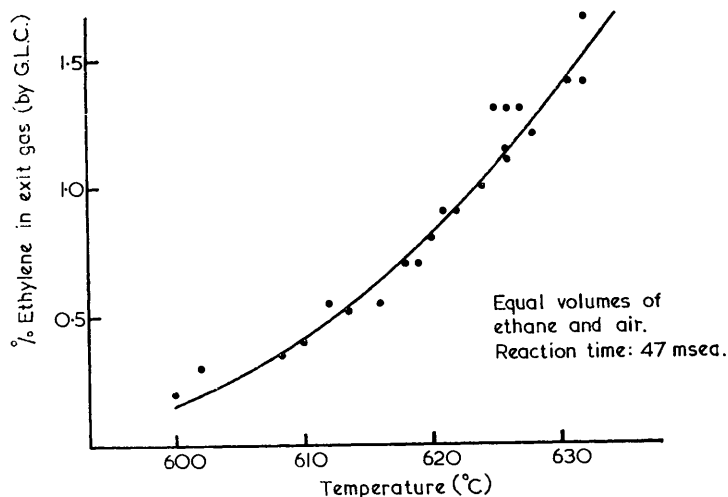* Corrected for decomposition in capillary.

FIG. 3. Formation of ethylene during oxidation of ethane.

Ethane and air, each, 250 l./hr.   The amounts of ethylene were determined by gas–liquid chromatography and corrected for the small amount present as impurity in the ethane.
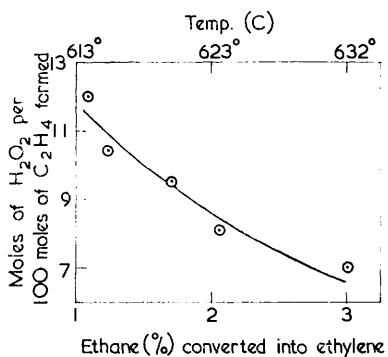

FIG. 4.   Yields of hydrogen peroxide on oxidation of ethane.
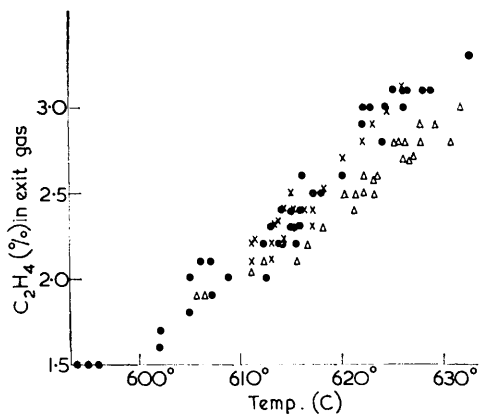

FIG. 5. Influence of partial pressure of oxygen on the yield of ethylene.

Ethane (in all cases), 250 l./hr.   (●) Air, 250 l./hr.   (×) Air, 187·5 l./hr., and oxygen, 62·5 l./hr.   (△) Air, 125 l./hr., and nitrogen, 125 l./hr.

Ethylene was determined by infrared spectroscopy at 10·55 μ.   The amount present as impurity in the ethane accounted for ~1·4% in the exit gas.

influence of the major product (ethylene) on the formation of minor products, ethylene (5 l./hr.) was fed in place of an equivalent quantity of ethane in a run at 626°; the yield of ethylene oxide increased, but any changes in the other products were inside experimental error, although the yields (relative to ethylene) of carbon monoxide and formaldehyde may have increased slightly and that of hydrogen may have decreased slightly. The influence of further added ethylene and of conversion on the yield of ethylene oxide was investigated (Table 3).

TABLE 3.

Formation of ethylene oxide.

Temp.	Conversion (%) $C_2H_6 \longrightarrow C_2H_4$	Ethylene (%)			Ethylene oxide, % in exit gas
		Initial *	Final	Average	
610°	0·84	0·13	0·5$_5$	0·3$_4$	<0·002
623	2·0	0·13	1·1$_5$	0·6$_3$	0·010 ± 0·004
626	2·6	0·1	1·4	0·7$_5$	0·017 ± 0·005
632	3·0	0·13	1·6	0·8$_8$	0·025 ± 0·005
626	2·6	1·3	2·6	1·9$_5$	0·024 ± 0·005
626	2·6	2·6	4·0	3·3$_5$	0·035 ± 0·005

* Includes ethylene present as an impurity.

The results on the influence of oxygen partial pressure are given in Fig. 5.

When acetaldehyde (equivalent to 4 mole % of the total gas admitted to the reactor) was included in the ethane feed there was a small increase in ethylene formation: at 615° the ethylene formed was equivalent to that formed in the absence of acetaldehyde at 620°. Separate experiments showed that thermal decomposition of acetaldehyde was negligible.

When nitrogen (250 l./hr.) and chlorine (5 l./hr.) were fed to the air-preheater, ethyl chloride was formed in high yield below 600°; when the nitrogen was replaced by air the chlorination was markedly retarded. The presence of chlorine only slightly enhanced ethylene formation during oxidation: in the region 600—610° the temperature required to convert a given proportion of the ethane into ethylene in the absence of the chlorine was less than 3° higher than when the chlorine was added. Bromine (5 l./hr.) behaved similarly, and hydrogen bromide (5 l./hr.) had at the most a slight sensitising effect on the oxidation of ethane.

DISCUSSION

The Basic Chain Mechanism.—The conditions of the present experiments are such that heterogeneous decomposition of hydrogen peroxide will be unimportant (see Appendix) although homogeneous decomposition (3) will occur,[11,12] leading to degenerate branching through (4):

$$M + H_2O_2 \longrightarrow M + 2HO\cdot \qquad \qquad . \; . \; . \; (3)$$
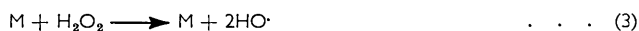
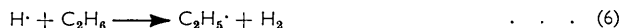$$HO\cdot + C_2H_6 \longrightarrow H_2O + C_2H_5\cdot \qquad \qquad . \; . \; . \; (4)$$

Then, if the basic chain is (1) + (2), and if the kinetic chain-length is not very short (say, at least 4 units), high yields of hydrogen peroxide should be isolated by the quench technique. This was not the case (Fig. 4 and Tables 1 and 2); hence it is evident that one or both of the following factors operate: (*a*) the chain-steps are not (1) and/or (*b*) the chain-length is very short.

The mechanism will be discussed in semi-quantitative kinetic terms, by means of the results for 623° where 2% of the ethane is converted into ethylene, as an illustration. Ethylene is the major organic product (Table 1) and in agreement with Knox[3] no plausible step leading to its formation, other than (2), can be envisaged. However, alternatives which must be considered are (5) followed by (6) or (7). Reaction (5) followed by (6) can be discarded immediately, because hydrogen is not formed in quantities comparable with those of ethylene and any form of attack which can be envisaged on hydrogen would occur

[11] Hoare, Protheroe, and Walsh, *Trans. Faraday Soc.*, 1959, **55**, 548.

[12] Baldwin and Brattan in " Eighth International Symposium on Combustion," Williams & Wilkins, Baltimore, 1962, p. 110.

at least as fast on ethane. It will be shown later that the reaction is in a quasi-stationary state and this feature of the reaction can be used to decide whether reaction (2), or (5) + (7),

$$C_2H_5 \cdot \longrightarrow C_2H_4 + H \cdot \qquad \qquad \cdots \quad (5)$$

$$H \cdot + C_2H_6 \longrightarrow C_2H_5 \cdot + H_2 \qquad \qquad \cdots \quad (6)$$

$$H \cdot + O_2 + M \longrightarrow HO_2 \cdot + M \qquad \qquad \cdots \quad (7)$$

predominates. The quasi-stationary concentration of ethyl radicals is $1 \cdot 3 \times 10^{-8}$ mole/l. (see Appendix), and the rate of formation of ethylene by reaction (5) is $k_5[C_2H_5 \cdot]$, *i.e.*, $2 \cdot 6 \times 10^{-4}$ mole l.$^{-1}$ sec.$^{-1}$ [the value of k_5 given by Kerr and Trotman-Dickenson [13] is 10^{14} exp $(-40,000/RT)$], but the observed rate of ethylene formation is $3 \cdot 1 \times 10^{-3}$ mole l.$^{-1}$ sec.$^{-1}$, and so oxidative dehydrogenation (2) predominates over pyrolysis of ethyl radicals (5). However, reactions (5) + (6) may account for part of the ethylene and some

$$2C_2H_5 \cdot \longrightarrow C_2H_4 + C_2H_6 \qquad \qquad \cdots \quad (5a)$$

$$2C_2H_5 \cdot \longrightarrow C_4H_{10} \qquad \qquad \cdots \quad (5b)$$

(probably most) of the hydrogen. The disproportionation (5a) of ethyl radicals can be ignored as a source of ethylene, since n-butane is a very minor product and at lower temperatures $k_{5b} > k_{5a}$.[13] The ratio k_{5a}/k_{5b} is certainly not very temperature-dependent, and may even decrease with increasing temperature.[13]

The radical $HO_2 \cdot$ is evidently the successor of $C_2H_5 \cdot$, but the small yields of hydrogen on the one hand and of hydrogen peroxide on the other preclude the cycling of reactions (8) + (6), or of reaction (1), respectively, with reaction (2) in chains of any appreciable length. The alternative fate (9) of $HO_2 \cdot$ is even less likely than (8), for it is endothermic [14] by 63 kcal. mole^{-1} and if it occurred as the major fate of $HO_2 \cdot$ there would be very rapid branching and an isothermal explosion would result. Another possible fate of the radical

$$HO_2 \cdot + M \longrightarrow H \cdot + O_2 + M \qquad \qquad \cdots \quad (8)$$

$$HO_2 \cdot + M \longrightarrow HO \cdot + O + M \qquad \qquad \cdots \quad (9)$$

$HO_2 \cdot$ is disproportionation (10). This is a termination step, removing two chain carriers, but it is potentially a source of two further carriers through reaction (3). The observed

$$2HO_2 \cdot \longrightarrow H_2O_2 + O_2 \qquad \qquad \cdots \quad (10)$$

main products (ethylene and water) are explicable if a high proportion of $HO_2 \cdot$ radicals undergo reaction (10) which would be followed by (3). If all the $HO_2 \cdot$ radicals undergo reaction (10), hydrogen peroxide would now be a chain-carrier instead of a degenerate-branching agent, and the system would behave in a truly steady-state fashion, represented by scheme (11):
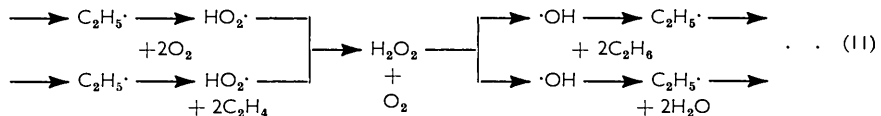
Clearly, the more likely situation is one involving a mixture of the chains represented by steps (1) + (2) and those represented by the cycle of events (11). Thus, after primary initiation [presumably (12)], which may be heterogeneous, a chain reaction of steps (1) and (2), with (3) as a source of chain-multiplication, would ensue effectively as an induction

$$C_2H_6 + O_2 \longrightarrow C_2H_5 \cdot + HO_2 \cdot \qquad \qquad \cdots \quad (12)$$
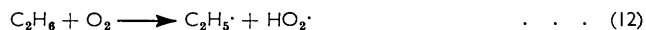
period. As the radical concentration increases, the chains become progressively shorter because the fate (10) of $HO_2 \cdot$ radicals competes more and more effectively with fate (1),

[13] Kerr and Trotman-Dickenson in " Progress in Reaction Kinetics," Vol. I, Pergamon, Oxford, 1961.
[14] P. Gray, *Trans. Faraday Soc.*, 1959, **55**, 488.

8 B

until ultimately the cycle (11) takes almost complete control. The experimental evidence concerning the extent to which (11) becomes dominant is from two sources. First, if an approach to sequence (11) does not occur until an appreciable proportion of the reaction time has elapsed, an increase in oxygen pressure should lead to a marked increase in the reaction rate, because it will shorten the pre-(11) period by causing a greater rate of primary initiation (12): it does not have this effect (Fig. 5). Secondly,.artificially included radical sources have little effect (see Results section). Thus the results are consistent with a reaction in which a quasi-stationary reaction condition (11) is reached in a time which is short compared with the reaction time. At this stage the chain-reaction involves four different carriers, one of which (H_2O_2) gives rise to a delayed propagation step. Comparison of the half-life of hydrogen peroxide (8 msec.; see Appendix) with the reaction time (47 msec.) shows that the number of complete cycles through which each chain passes is strictly limited.

Before discussing the mechanism further, the possibility of surface destruction, (13), of radical $HO_2\cdot$, which would also lead to the observed products, must be considered.

$$2HO_2\cdot \xrightarrow{\text{Wall}} H_2O + \tfrac{3}{2}O_2 \qquad \cdots \quad (13)$$

In the Appendix it is shown that the half-life of $HO_2\cdot$ towards reaction (10) is very short compared with the average time taken for a molecule to diffuse to the wall. Thus reaction (13) may be ignored.

The concentration of chains, and so the overall quasi-stationary rate, will depend upon the relative rates of reactions (1) and (10); if conditions are altered, thereby increasing (1)
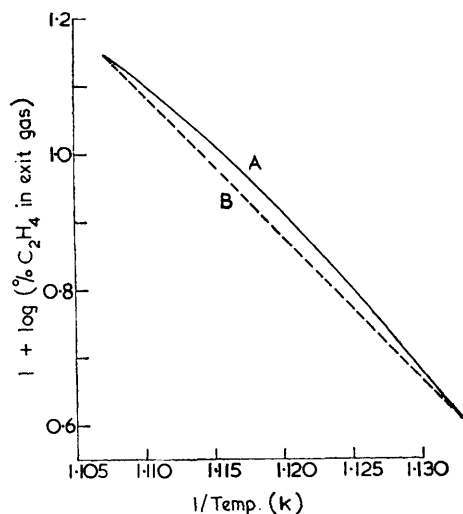

FIG. 6. (A) Arrhenius plot (from Fig. 3) for the formation of ethylene during oxidation of ethane. (B) Plot for $E = 95$ kcal. mole⁻¹.

The amounts of ethylene were corrected for the small amount present as impurity in the ethane.

relative to (10), there will be an increase in the quasi-steady concentration of radicals, and so in the overall rate. The present experiments extend over a temperature range of only 30° (Fig. 3), and since $E_1 \approx 13$ kcal. mole⁻¹ (see Appendix) and $E_{10} \approx 0$, the ratio k_1/k_{10} will not alter appreciably over this range; thus the quasi-stationary value of $[HO_2\cdot]$ will be nearly constant within the experimental range. The overall rate should then be determined by the rate at which hydrogen peroxide decomposes; E_3 is 46·3 kcal. mole⁻¹, and so the overall activation energy should also approximate to 46·3 kcal. mole⁻¹. Fig. 6 is an Arrhenius replot of Fig. 3 and shows that the average activation energy of the rate is 95 kcal. mole⁻¹; however the value falls to 70 kcal. mole⁻¹ at 3% conversion. The discrepancy between the expected and the apparent activation energy is likely to arise largely because a true steady-state reaction in which every $HO_2\cdot$ radical undergoes reaction (10) is never reached, but is approached asymptotically. At higher temperatures

(*i.e.*, higher extents of reaction) it is more nearly reached, and so branching is relatively less important, and the apparent activation energy here more nearly agrees with what would be expected if there were no induction period. The magnitude of the discrepancy between this hypothetical case and experiment is shown by taking the extent of reaction (1%) at 613° as basis; then the extent expected at 633° if the apparent activation energy is 46·3 kcal. mole^{-1} would be 1·8%. Actually it is 3·0%.

The extent to which the stationary state is approached can be gauged by comparing the rate of decomposition of hydrogen peroxide at the reactor outlet with the overall rate of ethane removal at 623°:

Final rate of formation of ·OH radicals through (3) = 2·6 × 10^{-3} mole l.$^{-1}$ sec.$^{-1}$ (see Appendix).

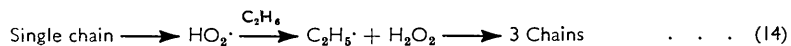Overall rate of consumption of ethane = 3·4 × 10^{-3} mole l.$^{-1}$ sec.$^{-1}$.

Again, the chain-length, ν, of the sequence (1) and (2), may be estimated:

$$\nu = \frac{\text{Rate at which HO}_2\text{· is removed in reaction (1)}}{\text{Rate at which HO}_2\text{· is removed in reaction (10)}}$$

$$= \frac{k_1[\text{HO}_2\text{·}][\text{C}_2\text{H}_6]}{2k_{10}[\text{HO}_2\text{·}]^2} = 0·10$$

(the values of k_1 and [HO$_2$·] are evaluated in the Appendix; the value of k_{10} is due to Burgess and Robb [15]).

Thus a chain reaction involving steps (1) + (2) is relatively unimportant; attack by the radical HO$_2$· on ethane is of minor importance from a very early stage in the reaction. That it cannot be ignored is shown in the three previous paragraphs.

When chain-carriers are removed by termination reactions, such as heterogeneous decomposition of hydrogen peroxide, the quasi-stationary condition will tend to re-establish itself since the fall in active centres will result in an intensified attack of radicals HO$_2$· on ethane, leading to branching (14):

$$\text{Single chain} \longrightarrow \text{HO}_2\text{·} \xrightarrow{\text{C}_2\text{H}_6} \text{C}_2\text{H}_5\text{·} + \text{H}_2\text{O}_2 \longrightarrow 3 \text{ Chains} \qquad \text{. . . (14)}$$

Multiplication of chains by primary initiation, (12), during the quasi-static stage, or by degenerate branching, *e.g.*, (15)

$$\text{CH}_2\text{O} + \text{O}_2 \longrightarrow \text{HO}_2\text{·} + \text{·CHO} \qquad \text{. . . (15)}$$

or by inclusion of radical sources, will have little effect since the system already contains a high concentration of active centres. Along with steps (14), such multiplication will tend to compensate for wastage of active centres.

The Formation of Minor Products.—The origin of the main products ethylene and water, and of hydrogen peroxide, has thus already been found, and a source of hydrogen, namely, reactions (5) + (6), has been suggested.
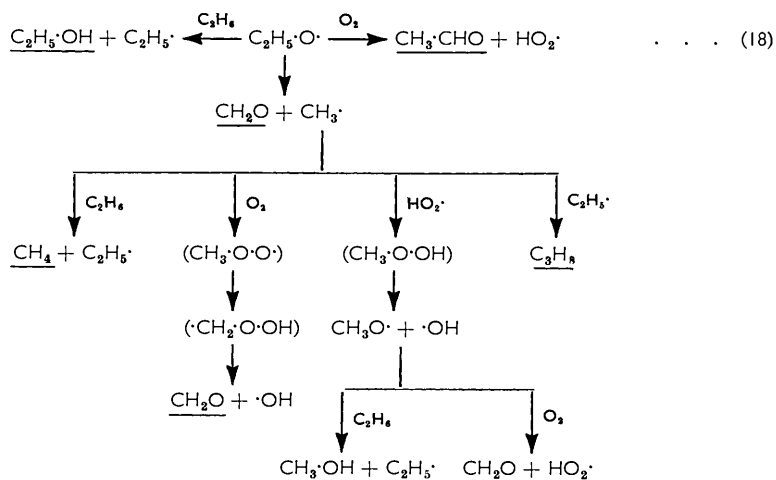
The quasi-stationary concentration of HO$_2$· radicals is about an order of magnitude greater than that of ethyl radicals (see Appendix). Hence the association (16), together with (17), might be expected to occur about an order of magnitude less frequently than reaction (10).

$$\text{C}_2\text{H}_5\text{·} + \text{HO}_2\text{·} \longrightarrow (\text{C}_2\text{H}_5\text{·O·OH}) \longrightarrow \text{C}_2\text{H}_5\text{O·} + \text{·OH} \qquad \text{. . . (16)}$$

$$\left.\begin{array}{l} \text{C}_2\text{H}_5\text{·} + \text{HO}_2\text{·} \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}_2 \\ \text{C}_2\text{H}_5\text{·} + \text{HO}_2\text{·} \longrightarrow \text{O}_2 + \text{C}_2\text{H}_6 \end{array}\right\} \qquad \text{. . . (17)}$$

Ethyl hydroperoxide is less stable than hydrogen peroxide; it will break down rapidly as in (16), even if it exists for a time longer than required for a "sticky" collision. The

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[15] R. H. Burgess and Robb, *Chem. Soc. Special Publ.* No. 9, 1958, p. 167.
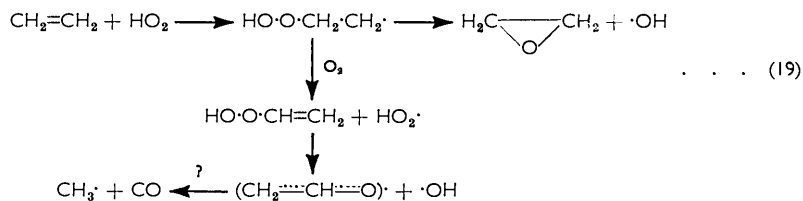
ethoxy-radical formed in reactions (16) would be expected to lead to some of the remaining observed products (18):

$$\underline{C_2H_5 \cdot OH} + C_2H_5 \cdot \xleftarrow{\ C_2H_4\ } C_2H_5 \cdot O \cdot \xrightarrow{\ O_2\ } \underline{CH_3 \cdot CHO} + HO_2 \cdot \qquad \cdots \quad (18)$$

$$\downarrow$$

$$\underline{CH_2O} + CH_3 \cdot$$

$$\underline{CH_4} + C_2H_5 \cdot \qquad (CH_3 \cdot O \cdot O \cdot) \qquad (CH_3 \cdot O \cdot OH) \qquad \underline{C_3H_8}$$
$$\xleftarrow{C_2H_4} \qquad \downarrow O_2 \qquad \downarrow HO_2 \cdot \qquad \downarrow C_2H_5 \cdot$$

$$(\cdot CH_2 \cdot O \cdot OH) \qquad CH_3O \cdot + \cdot OH$$

$$\downarrow$$

$$\underline{CH_2O} + \cdot OH$$

$$\underline{CH_3 \cdot OH} + C_2H_5 \cdot \qquad \underline{CH_2O} + HO_2 \cdot$$
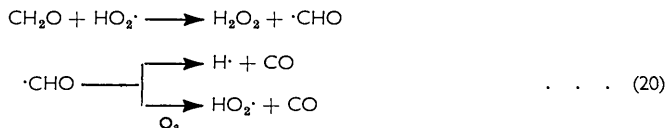$$\xleftarrow{C_2H_4} \qquad \qquad \downarrow O_2$$

It is suggested that the reactions of scheme (18) are the sources of the major proportion of the products shown (underscored).

The results in Table 3 indicate that a high proportion of the ethylene oxide has its origin in ethylene, presumably by $HO_2 \cdot$ attack on the double bond (19).

Although the experimental evidence is not clear-cut, a small proportion of the carbon monoxide and formaldehyde may arise through ethylene, and also ethylene may slightly lower the hydrogen yield, presumably by the reverse of reaction (5). A possible mode of formation of the carbon monoxide, formaldehyde, and methane through ethylene is shown in scheme (19); the methyl radical thus formed would react as in (18).

$$CH_2{=}CH_2 + HO_2 \longrightarrow HO \cdot O \cdot CH_2 \cdot CH_2 \cdot \longrightarrow H_2C\underset{O}{\overset{\diagup\diagdown}{\qquad}}CH_2 + \cdot OH$$

$$\downarrow O_2 \qquad \qquad \cdots \quad (19)$$

$$HO \cdot O \cdot CH{=}CH_2 + HO_2 \cdot$$

$$CH_3 \cdot + CO \xleftarrow{\ ?\ } (CH_2{\cdots}CH{\cdots}O) \cdot + \cdot OH$$

At least part of the carbon monoxide must arise through formaldehyde, *e.g.*, by reaction (20), and Table 2 shows that the importance of carbon monoxide increases with conversion, which is consistent with this mode of origin, as well as with (19).

$$CH_2O + HO_2 \cdot \longrightarrow H_2O_2 + \cdot CHO$$

$$\cdot CHO \xrightarrow{\qquad} \begin{array}{l} \longrightarrow H \cdot + CO \\ \longrightarrow HO_2 \cdot + CO \end{array} \qquad \cdots \quad (20)$$
$$O_2$$

n-Butane undoubtedly arises through dimerisation of ethyl (5b). No trace of butenes was detected; thus there was no evidence for reaction (21).

$$C_2H_5 \cdot + C_2H_4 \longrightarrow C_4H_9 \cdot \xrightarrow{\ O_2\ } C_4H_8 + HO_2 \cdot \qquad \cdots \quad (21)$$
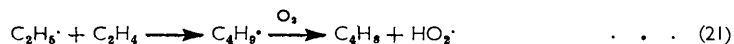
The present work suggests the importance of radical–radical reactions, especially self-disproportionation of $HO_2\cdot$, in oxidation of ethane above 600°: it is likely that this disproportion is of much wider occurrence in combustion phenomena. Thus it would be expected to play an important part in the combustion of more complicated fuels [16] which yield radicals which pyrolyse to give largely ethyl radicals. On the other hand, those fuels which give largely methyl radicals will less frequently lead to the disproportionation of $HO_2\cdot$ radicals as an important feature of their oxidation, for reaction (2) will be largely

$$CH_3\cdot + O_2 \longrightarrow CH_2O + \cdot OH \qquad \qquad \cdot \ \cdot \ \cdot \ (22)$$
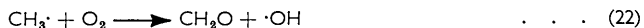
replaced by reaction (22) leading to the reactive $\cdot OH$ rather than to $HO_2\cdot$. The importance of disproportionation of radicals $HO_2\cdot$, and of homogeneous breakdown of hydrogen peroxide (3), has recently been demonstrated in the slow combustion of hydrogen.[17] Again, the relative rates of oxidation of a series of n- and iso-paraffins at 500—600° can be correlated with the number and type of C–H bonds each possesses; the latter should determine the level to which $[HO_2\cdot]$ builds before establishment of quasi-stationary conditions.[16]

APPENDIX

Derivation of Quantities used in the Discussion.

Reaction conditions: Temperature, 623°. Pressure, 1·1 atm.
Reactor volume, 18 ml. Reaction time, 47 msec.
Reactants: Air + ethane (equal volumes).

The Half-life of Hydrogen Peroxide.—Recent studies [11,12] on the homogeneous decomposition of hydrogen peroxide are in essential agreement with one another. The reaction obeys second-order kinetics (first-order in the peroxide, first-order in the activating species). For the present purpose it will be assumed that the mixture of substances present during oxidation of ethane has the same activating power as hydrogen peroxide itself. Then,[12]

$$k_3 = 1·02 \times 10^{15} \exp. (-46,300/RT),$$

and at 623° the half-life is 8 msec.

The Quasi-stationary Ethyl Concentration:

$$[C_2H_5\cdot] = [(\text{Rate of n-butane formation})/k_{5b}]^{\frac{1}{2}}.$$

Kerr and Trotman-Dickenson [13] consider that k_{5b} is given by

$$k_{5b} = 10^{11·2} \exp (-2000/RT),$$

whence $[C_2H_5\cdot] = 1·3 \times 10^{-8}$ mole l.$^{-1}$.

The Rate Constant for Attack of $HO_2\cdot$ on Ethane.—(a) *Activation energy.* The ethane C–H bond strength is $\sim$97 kcal.[7] and the H–O bond strength in hydrogen peroxide is $\sim$90 kcal.[6] Hence the abstraction reaction is about 7 kcal. endothermic and is likely to have E_1 close to 13 kcal. mole^{-1}. (b) *The A factor.* For abstraction [13] of primary hydrogen by simple radicals containing a few atoms, the factor A is about $10^{8·5}$. Thus, $k_1 = 10^{8·5} \exp (-13,000/RT)$, *i.e.*, $2·3 \times 10^5$ l. mole^{-1} sec.$^{-1}$ at 623°.
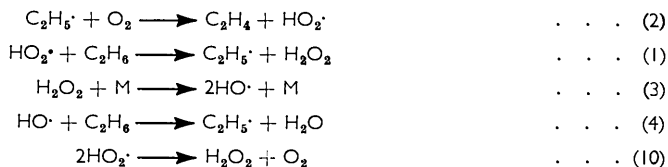
The Rate Constant for the Reaction $C_2H_5\cdot + O_2 \longrightarrow HO_2\cdot + C_2H_4$.—From the known rate constants for the pyrolysis of butyl radicals,[13] observations [16] on the high-temperature oxidation of n-butane, and the assumption that all the β-hydrogen atoms of ethyl, n-butyl, and s-butyl

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[16] Sampson, unpublished work.
[17] Baldwin and Mayor, *Trans. Faraday Soc.*, 1960, **56**, 80, 103; Baldwin, Doran, and Mayor in "Eighth International Symposium on Combustion," Williams & Wilkins, Baltimore, 1962, 103.

radicals are abstracted by oxygen at the same rate, it is deduced that $k_2 = 1\cdot0 \times 10^8$ l. mole^{-1} sec.$^{-1}$ at 623.*

The Quasi-stationary Concentration of $HO_2\cdot$ *Radicals.*—The basic features of the reaction have been seen to be compatible with the following equations:

$$C_2H_5\cdot + O_2 \longrightarrow C_2H_4 + HO_2\cdot \qquad \cdot \cdot \cdot \ (2)$$
$$HO_2\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + H_2O_2 \qquad \cdot \cdot \cdot \ (1)$$
$$H_2O_2 + M \longrightarrow 2HO\cdot + M \qquad \cdot \cdot \cdot \ (3)$$
$$HO\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + H_2O \qquad \cdot \cdot \cdot \ (4)$$
$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad \cdot \cdot \cdot \ (10)$$

If the reaction is assumed to be in a quasi-stationary condition $d[HO_2\cdot]/dt = 0$;

$$k_2[C_2H_5\cdot][O_2] = k_1[HO_2\cdot][C_2H_6] + 2k_{10}[HO_2\cdot]^2.$$

Using the values of k_1, k_2, and $[C_2H_5\cdot]$ derived above and the published value of k_{10},[15] we obtain $[HO_2\cdot] = 1\cdot2 \times 10^{-7}$ mole l.$^{-1}$. The value of $[HO_2\cdot]$ may be calculated by using in part different data; for, if it is again assumed that branching is of minor importance, that $HO_2\cdot$ disproportionation is the predominant mode of termination, and that the predominant mode of initiation is by hydroxyl radicals derived from hydrogen peroxide, then $2k_3[H_2O_2][M] = 2k_{10}[HO_2\cdot]^2$. Using the value of k_3 derived above and of k_{10} from the work of Burgess and Robb,[15] and putting $[H_2O_2]$ equal to the final hydrogen peroxide concentration, we have $[HO_2\cdot] = 1\cdot4 \times 10^{-7}$ mole l.$^{-1}$. The near-equivalence of the two values for $[HO_2\cdot]$ must be regarded as fortuitous in view of the approximations involved.

Half-life of $HO_2\cdot$ *towards Self-disproportionation.*—The rate of self-disproportionation is $2k_{10}[HO_2\cdot]^2$. By using the value of k_{10} given by Burgess and Robb [15] and the average of the values of $[HO_2\cdot]$ derived above, the half-life of $HO_2\cdot$ towards reaction (10) is found to be 4×10^{-2} msec.

Time for Diffusion of H_2O_2 *and* $HO_2\cdot$ *to the Reactor Walls.*—By combination of (a) the Smoluchowski equation [18] for the average number of collisions occurring when a molecule diffuses a distance x cm., (b) the calculated mean free path of hydrogen peroxide in the mixture, and (c) its r.m.s. velocity, the average time for a hydrogen peroxide molecule to diffuse a distance x in the reaction mixture is found to be x^2 seconds. The calculation, strictly, applies to diffusion in a gas free from flow; however, the type of flow within the present reactor is not likely to modify it appreciably. The diameter of the reactor is 2·0 cm., and thus a molecule of hydrogen peroxide at the centre will take about 1 sec. to reach the wall; one which is 0·25 cm. from the wall will reach it in about 60 msec. Since the homogeneous half-life of hydrogen peroxide is 8 msec., surface decomposition will be of minor importance.

The diffusion characteristics of a radical $HO_2\cdot$ should be similar to those of a molecule H_2O_2; its much shorter homogeneous half-life (see above) will result in its surface reactions' being even less important.

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* If the value of $[C_2H_5\cdot]$ derived for the present system is used, together with the observed rate of ethylene formation [restricted by 10% to allow for reaction (5)], a value of k_2 may be calculated, for the rate of ethylene formation by reaction (2) is $k_2[O_2][C_2H_5\cdot]$. The value of k_2 thus obtained is $1\cdot5 \times 10^8$ l. mole^{-1} sec.$^{-1}$, in reasonable agreement with the value derived above.

[18] Semenov, " Chemical Kinetics and Chain Reactions," Oxford Univ. Press, 1935.