169. *Competitive Oxidations. Part II.* The Lower Alkanes and Cyclopropane.*

By W. E. FALCONER, J. H. KNOX, and A. F. TROTMAN-DICKENSON.

The oxidation of binary mixtures containing methane, ethane, propane, cyclopropane, isobutane, and neopentane has been studied. The relative rates of removal of the hydrocarbons have been measured by gas-chromatography. The relative reactivites of different C–H bonds have been derived. Previous work is discussed, and the nature of the chain-carrying radicals considered.

STUDIES in oxidation of hydrocarbons ranging from the measurement of knock ratings to that of the rates of slow oxidation emphasise the important effect of structure. Cullis, Hinshelwood, and Mulcahy [1] measured such differences roughly by determining the rates of pressure rise in the oxidation of pairs of hydrocarbons under the same conditions. They recognised that differences in overall reactivity probably resulted from the combined effects of several processes, such as chain initiation, chain propagation, and chain branching. The detailed investigation of these component reactions is clearly important in elucidating the general mechanism of oxidation of hydrocarbons. In this work we have attempted to measure the relative rates of the chain-propagating reactions for a number of hydrocarbons.

The first products of oxidation of a hydrocarbon are likely to be alkyl radicals containing the same number of carbon atoms as the parent hydrocarbon. For most hydrocarbons there will be more than one such radical. These radicals can either decompose or react with oxygen, and their rates of formation can be found by determining the yields of products which are characteristic of the radicals initially formed. This approach has been used by Burt, Cullis, Larsen, and Minkoff,[2] and by Cullis, Hardy, and Turner.[3]

---

* Part I, Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

[1] Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117; Mulcahy, *ibid.*, p. 128.

[2] Burt, Ebeid, and Minkoff, *Nature*, 1957, **180**, 188; Burt, Cullis, Larsen, and Minkoff, Seventh Symposium on Combustion, Butterworths, London, 1959, p. 428.

[3] Cullis, Hardy, and Turner, *Proc. Roy. Soc.*, 1958, *A*, **244**, 573; 1959, *A*, **251**, 265.

The former measured the relative yields of OH and OD in the products from the oxidation of a number of deuteropropanes at 423°, using infrared spectroscopy. They found that the chance of a given secondary hydrogen atom's appearing in the products as OH was about twice that of a given primary hydrogen atom so appearing. They argued that initial attack at a given secondary C–H bond was twice as fast as initial attack at a primary C–H bond. Since water and hydrogen peroxide are the main hydroxyl-containing products their conclusion requires that both the hydrogen atoms in these products arise from the initial removal of hydrogen from propane. It is impossible to devise a plausible mechanism for which this is true. If one accepts the HO_2 chain mechanism for the high-temperature oxidation of propane,[4,5] the water and hydrogen peroxide should contain equal quantities of primary and secondary hydrogen atoms: the chance that a given secondary atom appears in the water is thus three times the chance that a given primary hydrogen atom so appears. The value obtained by Burt *et al.* is not far from this, but it indicates that considerable secondary oxidation must have taken place and that, in the later stages, oxidation to water of the hydrogen initially on primary carbon atoms predominates. The results give no information about the relative rates of initial attack at different positions in the propane molecule.

Cullis, Hardy, and Turner [3] determined the points of origin of the carbon in carbon monoxide and carbonyl groups formed in the oxidation of ^{14}C-labelled 2-methylpentanes (isohexane) at 242° and assumed that the relative yields gave the relative rates of initial attack at different points in isohexane. They assumed that all alkyl radicals initially formed gave rise to the appropriate hydroperoxide, and that in the subsequent reactions of the hydroperoxide the C–O bond remained unbroken. They also assumed that primary and secondary hydroperoxides gave carbon monoxide in the same proportion and that the tertiary hydroperoxide gave equal molar yield of (carbon monoxide + carbonyl compounds). Kirk and Knox [6] have shown that carbon monoxide arises in roughly equal yields (about 10%) on heterogeneous decomposition of ethyl, isopropyl, and t-butyl hydroperoxides. Carbonyl compounds are formed as a result of the homogeneous decomposition from pyrolysis of alkoxy-radicals. There is no reason to believe that the carbon in the carbon monoxide was that originally attached to the oxygen in the hydroperoxide, and one cannot add the yield of carbon monoxide to the yield of carbonyl to obtain the original amount of hydroperoxide. While it is conceivable that the yields of carbon monoxide may give a measure of the initial attack on the isohexane molecule, we do not as yet known enough about the mechanism of the oxidation at 242° to justify this conclusion.

There is therefore no reliable information about the relative rates of initial attack at different points in a given hydrocarbon undergoing oxidation in the gas phase.

Knox, Smith, and Trotman-Dickenson [7] estimated the rates of attack at different points in hydrocarbons from measurements of the rates of consumption of hydrocarbons in binary mixtures.

If two hydrocarbons R^1H and R^2H form alkyl radicals R^1 and R^2, and if these radicals eventually produce oxygenated radicals X^1 and X^2 which then attack the hydrocarbons, we can write four propagating reactions which remove the hydrocarbons:

$$\begin{array}{ll} X^1 + R^1H = X^1H + R^1 & k_{11} \\ X^2 + R^2H = X^2H + R^2 & k_{22} \\ X^2 + R^1H = X^2H + R^1 & k_{12} \\ X^1 + R^2H = X^1H + R^2 & k_{21} \end{array}$$

---

[4] Falconer and Knox, *Proc. Roy. Soc.*, 1959, *A*, **250**, 493.

[5] Satterfield and Wilson, *Ind. Eng. Chem.*, 1954, **46**, 1001.

[6] Kirk and Knox, *Trans. Faraday Soc.*, 1960, **56**, 1296.

[7] Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509; Seventh Symposium on Combustion, Butterworths, London, 1959, p. 126.

Experimentally we measure the relative rates of removal of the two hydrocarbons and obtain an experimental rate constant ratio given by

$$\frac{k_1}{k_2} = \frac{\log\{[R^1H]_{\text{initial}}/[R^1H]_{\text{final}}\}}{\log\{[R^2H]_{\text{initial}}/[R^2H]_{\text{final}}\}}$$

If $k_{11} \neq k_{12}$ and $k_{22} \neq k_{21}$ the experimental ratio k_1/k_2 will depend upon the composition of the mixture. The original work on propane–ethane and propane–isobutane mixtures showed that k_1/k_2 was independent of $[R^1H]/[R^2H]$, independent of $[O_2]$/[total RH] with less than 33% of oxygen, and independent of temperature from 274° to 495°. The present work, which uses the same experimental technique, has substantiated the findings of the earlier work but has revealed a dependence of k_1/k_2 upon oxygen concentration in mixtures containing more than 33% of oxygen.

RESULTS

Methane–Ethane.—The oxidation of methane–ethane mixtures was studied only at 495° since the rate of oxidation at lower temperatures was very low at accessible pressures. The study was complicated because methane is an important product of the oxidation of ethane, and in certain instances so much methane was thus formed that the methane content of the mixture actually increased. In order to minimise the effect of the methane formed from ethane, all mixtures studied contained at least as much methane as ethane. Studies of the oxidation of ethane alone showed that with oxygen pressures below about 100 mm. the methane yield was 16 ± 2% of the ethane initially present (see Table 1). At higher oxygen pressures, the yield of methane was dependent on pressure in mixtures of given $[O_2]/[C_2H_6]$ ratio falling to a minimum value of about 2% at high pressures. Addition of nitrogen had no significant effect. In view of this, experiments were carried out only under conditions where a 16% yield of methane was to be expected. An appropriate correction to the methane concentration was made in calculating *k*(methane)/*k*(ethane). The reproducibility of this ratio at constant oxygen concentration when $[CH_4]/[C_2H_6]$ varies between 4 : 1 and 1 : 1 is evidence for the validity of the practice.

TABLE 1. *Oxidation of ethane at* 495°.

No. of expts.	$\frac{[O_2]}{[C_2H_6]}$	$\frac{[N_2]}{\text{total press.}}$	Total press. (mm.)	$\frac{C_2H_4}{C_2H_6\ (\text{cons.})}$ *	$\frac{100CH_4}{C_2H_6\ (\text{cons.})}$ *
5	0·25	Nil	100—360	0·64	15 ± 2
5	0·48	0·32	110—400	0·59	17 ± 2
5	0·72	Nil	105—300	0·48	18 ± 2
1	1·50	,,	108	0·28	15·6
1	,,	,,	149	—	15·4
1	,,	,,	165	0·26	15·2
1	,,	,,	179	0·13	7·5 †
1	,,	,,	201	0·03	6·6 †
1	,,	,,	250	0·01	1·7 †
1	,,	,,	288	0·01	1·5 †
1	1·93	0·33	96	0·20	15·0
1	,,	,,	153	0·20	13·2
1	,,	,,	204	0·20	11·3
1	,,	,,	272	0·00	1·9 †
1	,,	,,	355	0·01	0·4 †

* C_2H_6 (cons.) is the amount of ethane consumed in a run.

† These values are not included in the average value used as a correction factor in calculating *k*(methane)/*k*(ethane).

The relative rate of consumption of methane and ethane under these conditions is strongly dependent upon $[O_2]$/[RH], but independent of the total pressure in a mixture of given composition (see Table 2 and Fig. 1).

Preliminary study of the oxidation of ethane alone showed that ethylene was a major product. The conversion of ethane into ethylene was almost independent of pressure for a given value of $[O_2]/[C_2H_6]$ with $[O_2]$ below 100 mm., but fell at higher oxygen pressures. The variation of the low-pressure conversion into ethylene with $[O_2]/[C_2H_6]$ is shown in Fig. 2. Extrapolation to zero $[O_2]/[C_2H_6]$ shows that in oxygen-weak mixtures about 80% of the ethane removed is converted into ethylene. This value is in general agreement with the known yields of olefins obtained in other high-temperature oxidations (*e.g.*, of propane; Satterfield and Wilson,[5] Falconer and Knox [4]). It also agrees with a figure obtained by Knox and Wells [8] for the initial conversion of ethane into ethylene at 360°. When $[O_2]$ exceeded 100 mm., the conversion into ethylene fell sharply with pressure. The ethylene yield was low when the amount of residual methane was also low.

TABLE 2. *Oxidation of methane–ethane mixtures at* 495°.

No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(CH_4)}{k(C_2H_6)}$	No. of expts.	Press. range (mm.)	$\frac{[CH_4]}{[C_2H_6]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(CH_4)}{k(C_2H_6)}$
4	188—363	2·0	0·26	0·07	2	187—327	2·0	0·96	0·19
5	211—353	2·0	0·38	0·08	3	237—318	4·0	1·03	0·20
6	111—352	2·0	0·49	0·12	4	153—290	2·0	1·05	0·19
3	255—339	4·0	0·50	0·13	3	203—303	2·0	1·90	0·36
6	133—422	1·0	0·55	0·13					

FIG. 1. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$. k(*cyclopropane*)/k(*ethane*) (○, ●, ◑); k(*methane*)/k(*ethane*) (+).

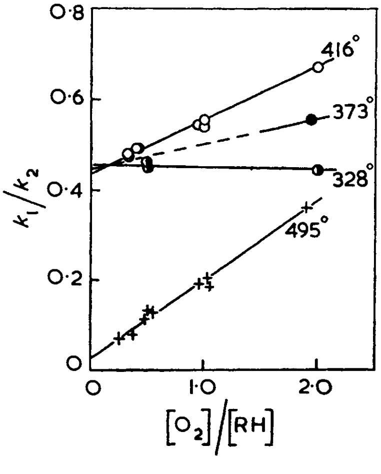
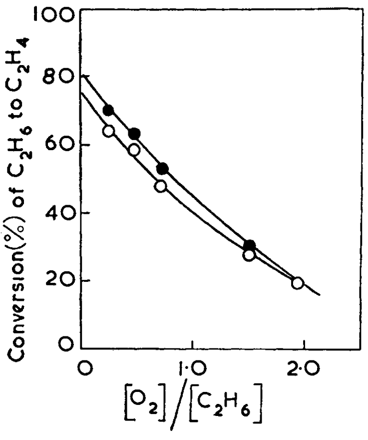


FIG. 2. *Dependence of the conversion of ethane into ethylene at* 495° *upon* $[O_2]/[C_2H_6]$. ○ *Average values for* $[O_2]$ = 100 *mm.* ● *Values for* $[O_2]$ = 0 (*extrapolated*).



Cyclopropane–Ethane.—The oxidation of this mixture is complicated by the possible isomerisation of cyclopropane to propene at higher temperatures. Below 416° less than 1% of the cyclopropane isomerised during a run. The relative rates of consumption were independent of $[O_2]/[RH]$ at 328° but increased markedly at 416° (Table 3, Fig. 1). The value (0·45) of k(cyclopropane)/k(ethane) at zero $[O_2]/[RH]$ is independent of temperature from 328° to 416°.

Ethylene was again a major product. The ethylene conversions for $[O_2]/[RH] = 0$ rose from about 60% at 328° to nearly 100% at 416°.

Ethane–Neopentane.—Neopentane is a particularly interesting hydrocarbon from the point of view of oxidation since no pentene can be formed from it by an HO_2 radical chain. Oxidation of neopentane might therefore involve radicals different from those taking part in the oxidations of other hydrocarbons, and there might be a strong dependence of the relative rates of removal on [Neopentane]/[Ethane]. Variation of this ratio over a six-fold range at 421° (Table 4) showed that this is not the case. The rate of removal of ethane relative to neopentane is independent of $[O_2]/[RH]$ at the lowest temperature (328°) but increases with $[O_2]/[RH]$ at

[8] Knox and Wells, unpublished results.

higher temperatures (Fig. 3). Whereas in the oxidations of methane–ethane and cyclopropane–ethane mixtures the ethane becomes relatively less reactive as $[O_2]/[RH]$ is increased, it becomes relatively more reactive in ethane–neopentane mixtures. For $[O_2]/[RH] = 0$, the relative rates of removal are given by:

$$k(\text{ethane})/k(\text{neopentane}) = 0{\cdot}14 \exp(1600/\boldsymbol{R}T)$$

A brief study of the oxidation of neopentane alone at 495° showed that although no pentene was formed, isobutene was a major product. It is presumably formed by the pyrolysis of the neopentyl radical: $\cdot CH_2{\cdot}CMe_3 \longrightarrow CH_2{:}CMe_2 + Me\cdot$. In the competitive oxidations, the proportion of neopentane converted into isobutene increases with temperature, probably because the decomposition of the neopentyl radical has a higher activation energy than its oxidation.

TABLE 3. *Oxidation of cyclopropane–ethane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_3H_6]/[C_2H_6]$	[Oxygen]/[Hydrocarbon]	$k(C_3H_6)/k(C_2H_6)$
3	328°	200—390	2·0	0·49	0·46
8	328	104—360	0·5	0·50	0·45
9	328	110—442	1·0	2·00	0·44
3	373	176—245	2·0	1·96	0·55
4	416	98—355	0·33	0·33	0·48
5	416	85—293	3·0	0·35	0·47
8	416°	79—403	3·0	0·50	0·49
4	416	114—405	0·33	0·51	0·49
2	416	188—325	1·0	0·95	0·54
5	416	89—430	3·0	1·00	0·54
7	416	85—437	0·33	1·00	0·55
6	416	260—456	1·0	2·00	0·67

TABLE 4. *Oxidation of ethane–neopentane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$[C_2H_6]/[C_5H_{12}]$	[Oxygen]/[Hydrocarbon]	$k(C_2H_6)/k(C_5H_{12})$
3	328°	230—320	1·0	0·33	0·53
4	328	180—330	2·0	0·64	0·51
5	328	245—390	2·0	1·50	0·54
3	328	270—405	2·0	2·96	0·54
5	421	180—330	2·0	0·25	0·47
4	421	205—320	0·5	0·25	0·48
6	421	160—300	1·0	0·50	0·48
7	421	170—405	3·0	0·50	0·49
5	421	130—380	0·5	0·50	0·48
5	421	200—400	2·0	0·82	0·51
5	421°	185—425	2·0	1·22	0·54
4	421	210—310	0·5	1·26	0·53
4	421	180—340	2·0	2·00	0·59
5	421	250—390	2·0	2·92	0·73
3	495	210—370	2·0	0·25	0·40
3	495	160—315	0·5	0·50	0·46
3	495	225—365	2·0	0·50	0·43
3	495	175—290	2·0	1·00	0·51
3	495	225—290	2·0	2·06	0·66

Neopentane–Isobutane.—Only 1 : 1 mixtures were investigated (Table 5). At 326° there was no dependence upon $[O_2]/[RH]$, but at higher temperatures the neopentane became relatively more reactive as $[O_2]/[RH]$ was increased (Fig. 3). For $[O_2]/[RH] = 0$, the relative rates of oxidation are given by:

$$k(\text{neopentane})/k(\text{isobutane}) = 0{\cdot}26 \exp(1000/\boldsymbol{R}T)$$

for the range 328—495°. Isobutene is a major product of the oxidation of both isobutane and neopentane.

The oxygen-dependence for this and the previous mixture indicates that there should be a strong oxygen-dependence in the ethane–isobutane oxidation.

Propane–Isobutane.—The results of a number of experiments carried out by Smith on this mixture are recorded in Table 6. The range of oxygen concentration is too small to disclose any dependence upon $[O_2]/[RH]$. The mean value of $k(\text{propane})/k(\text{isobutane})$ between 310° and 420° is 0·67.

Ethane–Propane.—This system was extensively studied by Knox, Smith, and Trotman-Dickenson[7] with mixtures in which $[O_2]/[RH]$ was less than 0·50. In this region no dependence upon $[O_2]/[RH]$ was noted. A few experiments with much higher $[O_2]/[RH]$ ratios summarised

TABLE 5. *Oxidation of neopentane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_5H_{12}]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_5H_{12})}{k(C_4H_{10})}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_5H_{12}]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_5H_{12})}{k(C_4H_{10})}$
2	326°	255—365	1·0	0·52	0·61	2	492°	265—295	1·0	0·33	0·57
2	326	235—295	1·0	1·50	0·63	2	492	160—180	1·0	1·00	0·66
						2	492	165—180	1·0	2·00	0·69
2	421	195—330	1·0	0·35	0·59						
2	421	275—345	1·0	1·00	0·68						
2	421	270—285	1·0	2·45	0·73						

TABLE 6. *Oxidation of propane–isobutane mixtures.*

No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_8]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_8)}{k(C_4H_{10})}$	No. of expts.	Temp. (°c)	Press. range (mm.)	$\frac{[C_3H_8]}{[C_4H_{10}]}$	$\frac{[\text{Oxygen}]}{[\text{Hydrocarbon}]}$	$\frac{k(C_3H_8)}{k(C_4H_{10})}$
5	310°	140—420	1·0	0·50	0·66	3	420°	170—400	1·0	0·50	0·60
4	310	180—315	3·0	0·50	0·70	2	420	155—245	0·33	0·50	0·73
3	420	145—335	0·33	0·40	0·68	3	420	155—345	3·0	0·75	0·68

in Table 7, show that the dependence upon $[O_2]/[RH]$ is comparable with that in the neopentane–ethane system. The ethane appears more reactive as $[O_2]/[RH]$ is raised. Thus the relative oxidation rates of propane and neopentane should be nearly independent of $[O_2]/[RH]$.

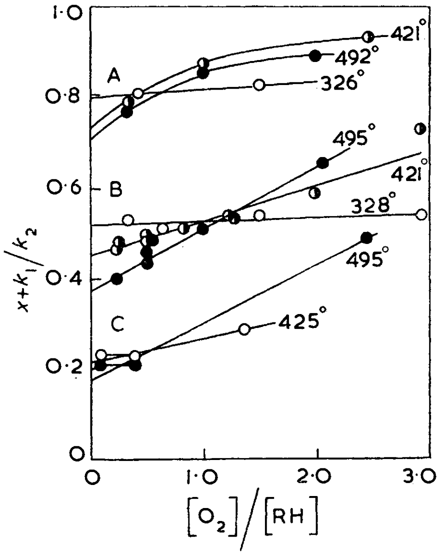


FIG. 3. *Variation of the relative rates of oxidation with* $[O_2]/[RH]$.
(A), k(neopentane)/k(isobutane), $x = 0{\cdot}20$;
(B), k(ethane)/k(neopentane), $x = 0$;
(C), k(ethane)/k(propane), $x = -0{\cdot}20$.

Additives.—One of the most striking effects noted in the present work is the relative independence of the relative rates of oxidation on $[O_2]/[RH]$ at low temperatures and the very marked effect of changes in this ratio at 400° and above. These results can indicate only that the products play an important part in governing the composition of the free-radical mixture which removes the parent hydrocarbons in the later stages of oxidation at higher temperatures. With this in mind, experiments were carried out with ethane–propane mixtures to ascertain whether any of the more probable initial products could account for the change.

The results presented in Table 7 show that addition of ethylene, propene, methanol, or formic acid has no measurable effect at 425°. Hydrogen and formic acid were likewise ineffective at 495°.

Acetaldehyde, normally regarded as a potent accelerator of oxidations, had only a slight effect at 495° and no effect at 425°. At 495°, 10% was required to give a moderate increase in k(ethane)/k(propane). This amount is far in excess of that likely to be present in the oxidations, and its effect is considerably less than that obtained by adding more oxygen. We therefore have no direct experimental evidence as to the cause of the marked dependence of the relative oxidation rates on the oxygen to hydrocarbon ratio. It is not caused by the oxidation of any of the products mentioned above.

During the study of the effect of addition of ethylene it was noted that the ethane consumption was sometimes unexpectedly small. This was shown to be due to the formation of saturated hydrocarbons from the last stages of the oxidation of the olefin. As is shown in Table 8, up to 11% of the ethylene can be converted into ethane during the later stages of its oxidation at high temperatures. If, however, the reaction mixture is removed from the reaction vessel before the oxygen is exhausted, the conversion into saturated hydrocarbon is greatly reduced. With propene, both ethane and propane are formed. It is clear, therefore, that transfer of hydrogen to the olefin occurs, and that this is followed by abstraction of a hydrogen atom by the alkyl radical thereby formed. A suggested reaction is:

TABLE 7. *Effect of additives on ethane–propane oxidations at 425° and 495°.*

No. of expts.	Additive	[Oxygen]/[Hydrocarbon]	Temp. (°c)	$k(C_2H_6)/k(C_3H_8)$
—	None	<0·50	425°	0·43 [7]
2	None	1·35	425	0·49
3	40% C_2H_4	0·25	425	0·45
2	50% C_2H_4	0·25	425	0·43
2	23% C_2H_4	1·35	425	0·51
3	23% C_3H_6	0·50	425	0·43
3	26% CH_3·OH	0·47	425	0·41
3	6% H·CO_2H	0·57	425	0·45
—	None	<0·50	495	0·41 [7]
1	None	0·34	495	0·41
2	None	2·45	495	0·79
2	2% CH_3·CHO	0·34	495°	0·45
2	11% CH_3·CHO	0·50	495	0·54
2	25% CH_3·CHO	0·33	495	0·53
2	10% CH_3·CHO 10% C_2H_4	0·42	495	0·52
2	10% CH_3·CHO 10% C_3H_6	0·41	495	0·51
1	6% H·CO_2H	0·42	495	0·39
2	19% H_2	0·34	495	0·41

TABLE 8. *Oxidation of olefins at 425° and 495°.*

Olefin	[Oxygen]/[Olefin]	Extent of reaction	Temp. (°c)	100 C_2H_6/Olefin (cons.) *	100 C_3H_8/C_3H_6 (cons.)
C_2H_4	0·50	Complete	425°	8	—
	0·50	2/3 complete	425	0	—
	0·50	Complete	495	11	—
	0·50	2/3 complete	495	2	—
C_3H_6	0·50	Complete	425	2·5	3·5
	0·50	2/3 complete	425	0	0

* Olefin (cons.) is the amount of olefin consumed in a run.

$$C_2H_4 + HO_2 = C_2H_5 + O_2$$

Hydrogen abstraction will only occur when the oxygen concentration is very low. Alternatively, two alkyl radicals can disproportionate to form molecules of alkane and olefin.

DISCUSSION

The main experimental findings may be summarised as follows: (1) All the oxidations studied show the same basic features. (2) The overall relative rate constants k_1/k_2 do not depend upon $[R^1H]/[R^2H]$. (3) The ratios k_1/k_2 are independent of $[O_2]/[RH]$ at 328°, but are dependent on it at temperatures above 400°. As $[O_2]/[RH]$ increases the values tend to unity. (4) The temperature variations of k_1/k_2 at zero $[O_2]/[RH]$ are slight. The largest temperature effect was for the ethane–neopentane mixture, for which the activation energy difference was about 1·6 kcal. mole^{-1}. (5) While the overall rates of oxidation of hydrocarbons differ greatly, the relative rates of oxidation in mixtures studied differ by factors of not more than 2 in all cases except methane–ethane.

The independence of the relative rate constants on $[R^1H]/[R^2H]$ indicates that the reactivities of the propagating radicals derived from different hydrocarbons are identical. In terms of the mechanism given in the introduction, $k_{11} = k_{12}$, and $k_{22} = k_{21}$. This applies over the whole temperature range and at all ratios of oxygen to hydrocarbon, even when the value of k_1/k_2 depends upon $[O_2]/[RH]$.

TABLE 9. *Relative reactivites of saturated hydrocarbons.*

Attacking radical:	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methane	0·6	0·02	0·03	0·05	—	0·03	0·002
Ethane	1	1	1	1	1	1	1
Propane	1·4	2·0	2·3	3·0	3·3	3·3	43
Cyclopropane	0·9	0·03	0·45	—	0·3	0·55	—
Isobutane	1·7	2·0	3·6	7·5	5·3	10	1050
Neopentane	1·8	2·1	2·0	1·5	1·5	1·7	0·75
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

* " Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

It has been shown [4,9] that variation of the oxygen concentration in the oxidation of propane between 320° and 480° has little effect upon the yields of the major products formed in the initial stages of reaction. The effect of oxygen is basically to increase the extent of reaction and thereby to alter the nature of the final products. The effect of $[O_2]/[RH]$ on k_1/k_2 at the higher temperatures does not therefore necessarily reflect any change in the initial rates of removal of the two hydrocarbons. It is more likely that the rates of removal in the later stages of reaction differ. This implies that the nature of the radical or radicals that remove the hydrocarbons changes as the reaction proceeds.

Analytical evidence presented here and elsewhere shows that in the early stages of oxidations the olefins corresponding to the original hydrocarbon are the major initial products. The only chain scheme that satisfactorily explains this is an HO_2 radical chain:

$$\text{Alkyl radical} + O_2 = \text{Olefin} + HO_2$$

$$\text{Alkane} + HO_2 = \text{Alkyl radical} + H_2O_2$$

It therefore seems likely that the values of k_1/k_2 that we have obtained by extrapolation to zero oxygen concentration apply to the HO_2 radical. This could be checked in detail by measurement of the initial olefin yields in competitive oxidations. The relative reactivites obtained (Table 9) may be compared with the relative reactivities of other radicals which have been studied in competitive systems.[10-15] The radical operative in oxidations is of relatively high reactivity, comparable with that of a chlorine atom [10] or a methoxyl radical.[11] The radical is less reactive than a fluorine atom [13] and more reactive than a methyl radical.[14] The identification of the radical in oxidations as HO_2 suffers from the difficulty that the commonly accepted strength [16] of the first O–H bond in hydrogen peroxide is 89·5 kcal., whereas the observed reactivities must be attributed to a radical that forms a bond of about 100 kcal. mole^{-1} with a hydrogen atom.

With chlorine [10] and bromine [12] atoms and with methyl radicals,[14] the reactivity does

---

[9] Knox, *Trans. Faraday Soc.*, 1960, **56**, 1225.

[10] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

[11] Shaw and Trotman-Dickenson, *J.*, 1960, 3210; Berces and Trotman-Dickenson, unpublished results.

[12] Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 1064.

[13] Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469; Anson, Fredricks, and Tedder, *J.*, 1959, 918; Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260; Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 4177.

[14] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.

[15] Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103; Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.

[16] Foner and Hudson, *J. Chem. Phys.*, 1955, **23**, 1364.

not vary much from one hydrocarbon to another for bonds of a given order. It is therefore reasonable to assume that this holds approximately for the radical involved in oxidations, and hence to derive the relative reactivities in Table 10. Apart from the expected trend in the direction of primary, secondary, and tertiary, it is notable that the CH bond of cyclopropane is about 8 times less reactive than a normal secondary bond, and the CH in methane about 20 times less reactive than a normal primary bond.

The identity of the radical or radicals responsible for the removal of hydrocarbon in the later stages of oxidation is not at all clear. Studies of propane oxidation [4,9] show that a major feature of the oxidation in the later stages is the removal of olefin. It appears that olefins react much faster than saturated hydrocarbons of the same carbon number. It was therefore possible that addition of olefin could induce behaviour characteristic of a mature reaction from the start of an oxidation. The experiments in which ethylene and propene were added to ethane–propane mixtures showed that this was not the case. Even the addition of acetaldehyde had little effect. The product from which the later-stage radicals are derived is therefore still uncertain but might be formaldehyde. From the fact that there is no dependence of the *k* ratio upon the relative concentrations of the two hydrocarbons, we deduce that the important radicals at this stage are not characteristic of the hydrocarbons forming them. Since this applies even to methane–ethane mixtures, it is likely that the radical contains at most one carbon atom. We are therefore limited to OH, CHO, CH_3, $CH_3·O$, and $CH_3·O·O$. The absence of methane as a product, except at the very end of the reactions, suggests that methyl radicals are oxidised before they have time to abstract hydrogen. The formation of methanol [17] suggests that methoxyl radicals are present, but the relative reactivities of the hydrocarbons with them,[11] as with methyl radicals,[14] do not correspond to those observed. The low strength of the H–CHO bond eliminates formyl radicals. Alkylperoxy-radicals seem unlikely for several reasons. They would be expected to behave very like hydroperoxy-radicals. They would be expected to be present at low temperatures and should, if they are highly reactive, be the chain carriers. Further, preliminary results indicate that their reactivities do not meet the requirements. Hence we conclude that hydroxyl radicals are the most probable chain carriers responsible for removal of the saturated hydrocarbons in the later stages of the reactions at high temperatures.

TABLE 10. *Relative reactivities of hydrogen atoms.*

	Relative reactivity towards:						
Type of H atom	F	Cl	Oxid.*	CF_3	MeO	CH_3	Br
Methyl	0·8	0·03	0·05	0·08	—	0·04	0·002
Cyclopropyl	0·9	0·03	0·45	—	0·29	0·55	—
Primary	1	1	1	1	1	1	1
Secondary	1·2	3	4	6	8	7	250
Tertiary	1·4	3	11	36	26	50	6300
Temp.	25°	250°	350°	182°	250°	182°	98°
Ref.	12	10	7	15	11	14	13

" Oxid." refers to the chain-carrying radical in oxidations when $[O_2]/[RH] = 0$.

EXPERIMENTAL

Materials.—Methane, ethane, cyclopropane, isobutane, and neopentane were obtained from cylinders, thoroughly degassed, and stored in 2-l. bulbs. The ethane used in ethane–cyclopropane and ethane–methane oxidations was passed through a column packed with a mercuric acetate–mercuric nitrate–ethylene glycol solution supported on 20—30-mesh firebrick [18] to remove the ethylene present in the cylinder gas; that used in neopentane–ethane oxidations was freed

---

[17] Pease, *J. Amer. Chem. Soc.*, 1938, **60**, 2244; Bailey and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 311; Knox and Norrish, *ibid.*, 1954, *A*, **221**, 151.

[18] Kerr and Trotman-Dickenson, *Nature*, 1958, **182**, 466.

from ethylene by passing it through sulphuric acid and charcoal saturated with bromine. Bromine vapour and bromides were removed by 30% *NN*-dimethyl-*p*-toluidine supported on 40—60-mesh firebrick. Ethylene and propene were free from ethane and propane. Analysis of the hydrocarbons showed them to be better than 99·5% pure. Oxygen was obtained from B.O.G. cylinders. The acetaldehyde used as an initiator was of " AnalaR " quality.

Apparatus and Procedure.—Oxidations were carried out in a conventional static high-vacuum apparatus. The reaction vessel (107 ml.; Pyrex) was enclosed in an electric furnace controlled by a thermostat to ±1°; the temperature along the length of the reaction vessel was constant within 1°.

The hydrocarbons and oxygen, measured in a constant-volume gas burette, were mixed before each series of runs. Some mixture was allowed to enter the pre-heated reaction vessel, and the initial pressure of the gases was noted on a mercury manometer. The reactions were followed by the pressure rise on the manometer and when this rise had ceased the condensable gases were frozen into a sampling tube at −183° for analysis; the non-condensable gases were pumped off. In order to analyse mixtures containing methane, the sampling tube was packed with activated alumina to condense the methane. Samples were normally withdrawn after the reaction had run to completion. However, k_1/k_2 was independent of the extent of reaction beyond 80%. Small quantities of acetaldehyde introduced as an initiator in some of the low-temperature oxidations of ethane–cyclopropane mixtures had no effect on the observed rate constant ratio.

Analysis.—Analysis was by gas chromatography, carbon dioxide being used as the carrier gas; the gases were determined with a Janak nitrometer.[19]

Ethane, ethylene, and cyclopropane were separated on an 80-cm. column of silver nitrate–ethylene glycol–30—40 mesh firebrick [20] followed by 280 cm. of 40—60-mesh activated alumina poisoned with $\frac{3}{4}$% of squalane.

Methane, ethane, and ethylene were separated with split columns. The first column consisted of 80 cm. of the silver nitrate mixture followed by 160 cm. of poisoned alumina. The second was 240 cm. of Sutcliffe and Speakman's 32—40-mesh activated charcoal. During analysis the two columns were at first connected in series, and the methane and other permanent gases eluted on to the charcoal column and isolated. The ethane and ethylene were then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal column.

For ethane, ethylene, isobutene, and neopentane a three-section column was employed. The first section was 240 cm. of 20% nitrobenzene on 52—72-mesh firebrick; the second, 80 cm. of silver nitrate mixture followed by 160 cm. of poisoned alumina; the third 120 cm. of the silver nitrate mixture. In analysis, sections one and two were first connected in series, and carbon dioxide passed until the ethane and ethylene were isolated on the second section of the column. Sections one and three were then connected in series, and the isobutene and neopentane eluted directly into the detector. Finally, the ethane and ethylene were eluted from section two.

Isobutene, isobutane, neopentane, and the C_2 and C_3 hydrocarbons were separated as follows: The contents of the sample tube were eluted on to a column of 10 cm. of poisoned alumina followed by 230 cm. of 20% nitrobenzene on firebrick, and the C_2 and C_3 hydrocarbons were eluted into the atmosphere. The column was then connected in series with 120 cm. of silver nitrate mixture, and the C_4 and C_5 hydrocarbons were eluted.

All columns were operated at room temperature. Standardisation runs were carried out for each furnace temperature, the normal procedure being used for an oxidation, but with omission of the oxygen from the original mixture. In this way systematic errors of calibration were eliminated. The accuracy of the analytical results was about ±1%.

This work has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Research Office.

CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY.

[*Received, July* 25*th*, 1960.]

---

[19] Janak, *Coll. Czech. Chem. Comm.*, 1954, **19**, 684, 917.

[20] Bednas and Russell, *Canad. J. Chem.*, 1958, **36**, 1272.