AD-A092 931 HULL UNIV (ENGLAND) DEPT OF CHEMISTRY F/G 7/3
KINETICS OF HYDROGEN-OXYGEN AND HYDROCARBON-OXYGEN REACTIONS.(U)
JUN 80 R B BALDWIN, R W WALKER AFOSR-77-3215
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INTERIM SCIENTIFIC REPORT

GRANT NO. AFOSR-77-3215

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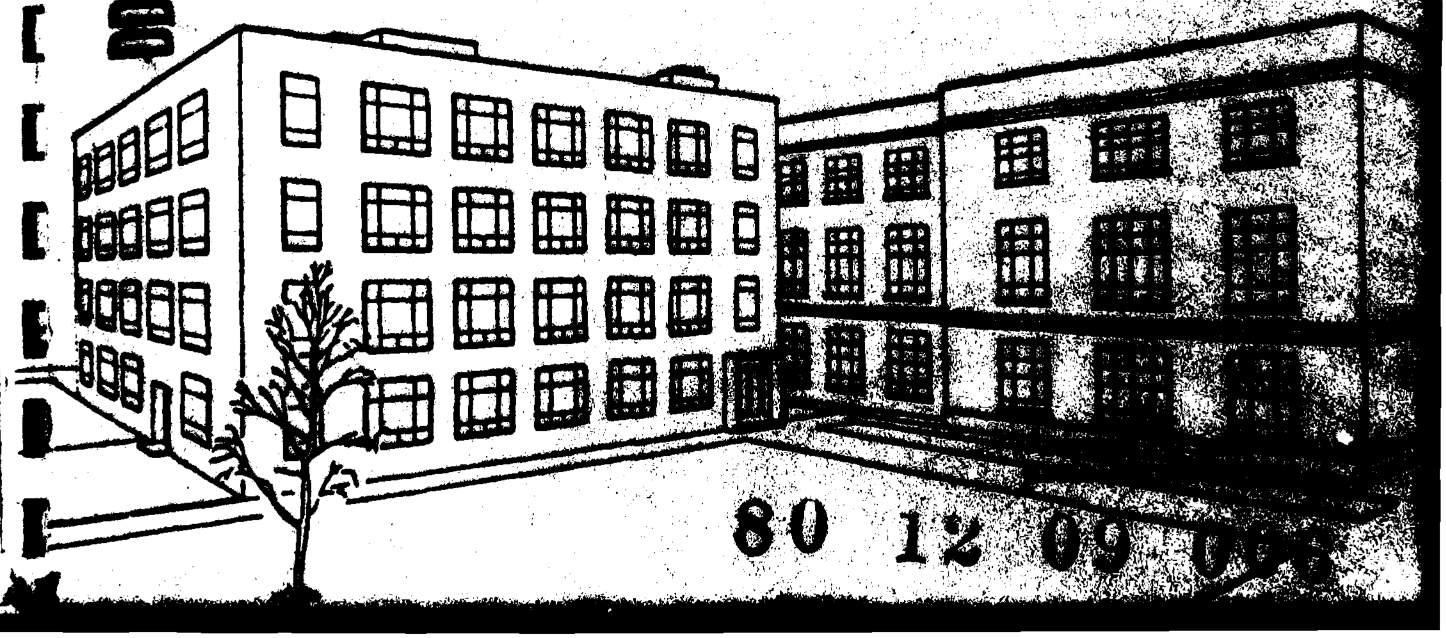

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) UNCLASSIFIED

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (19) (18) AFOSR-TR- 80 - 1243 2. GOVT ACCESSION NO. AD-A092 931	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) KINETICS OF HYDROGEN-OXYGEN AND HYDROCARBON-OXYGEN REACTIONS	5. TYPE OF REPORT & PERIOD COVERED Interim 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) ROBERT R. BALDWIN RAYMOND W. WALKER (11) 30 Jun 80 (15)	8. CONTRACT OR GRANT NUMBER(s) AFOSR-77-3215
9. PERFORMING ORGANIZATION NAME AND ADDRESS DEPARTMENT OF CHEMISTRY THE UNIVERSITY OF HULL HULL, HU 6 7RX, ENGLAND (12) 62l	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) 2308/B2 (17) B2 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BUILDING 410 BOLLING AFB, DC 20332	12. REPORT DATE June 30, 1980 13. NUMBER OF PAGES 54
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) (9) Interim scientific rept. 1 Apr 77-30 Jun 80	15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

1. RAte constants of the $H_2 + O_2$ reaction at 500°C have been refined. 2. Rate onstants and Arrhenius parameters for reactions of H atoms and OH radicals with C2-C5 alkanes, 2,2,3,3-tetramethylbutane (TMB) and 2,2,3-trimethylbutane (TRIMB) ave obtained. Detailed studies have been made of the products from the oxidation f i-butane, n-pentane, TMP and TRIMB. Rate constants for R + O_2 =conjugate alkene, for homolysis of R radicals, and for the isomerisation of RO_2 radicals to hydroperoxyalkyl radicals have been tabulated for a range of radicals. 3. Preliminary studies have been made of the oxidation process of alkenes. 4. Rate constants for reactions involved in the oxidation of propionaldehyde and of -

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isobutyraldehyde have been listed. 5. The decomposition of TMB in the presence of O2 has been used to study the reaction of HO2 radicals with TMB, C_2H_6, and with CO, and the reaction of C_2H_5 and t-C_4H_9 radicals. 6. The decomposition of TRIMB in the presence of O2 has enabled the thermochemistry of t-C_4H_9 and i-C_3H_7 radicals to be examined. 7. Interpretation of the N_2O - H_2 reaction has continued.

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AFOSR-TR-1243

Block 19 Key words / continued

Effect of surface in combustion reactions
Reaction of OH and hydroperoxy radicals with CO
Rate constants for H plus hydrocarbon
Rate constants for OH plus hydrocarbon
Rate constants for reactions of alkyl radical with oxygen
Oxidation of propionaldehyde, isobutyraldehyde
Rate constants for hydroperoxy radical plus hydrocarbon
Rate constant for initiation process in aldehyde oxidation
Reaction of H atoms with hydroperoxy radical
Decomposition of tetramethylbutane
Mechanism of hydrogen and nitrous oxide reaction
Thermochemistry of t-butyl radicals
Thermochemistry of i-C3H7 radicals
Rate constants for hydroperoxy radical with aldehydes
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Carbon dioxide formation in oxidation of propionaldehyde and isobutyraldehyde
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Molecular decomposition of tetramethylbutane

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GRANT AFOSR-77-3215 30th JUNE 1980

INTERIM SCIENTIFIC REPORT

Kinetics of Hydrogen-Oxygen and Hydrocarbon-Oxygen Reactions

1st April 1977 - 30th June 1980

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by Baldwin, R. R., and Walker, R. W.

Chemistry Department,
The University,
HULL.

The research reported in this document has been sponsored by, or in part by, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Grant No. AFOSR-77-3215.

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INTRODUCTION

The reaction of a hydrocarbon with oxygen is a complex process involving the formation of a large number of products which themselves influence the oxidation, particularly as they are usually more reactive than the parent material. As a consequence, the whole process is highly autocatalytic under many conditions, and the nature and concentration of the radicals vary sharply as the reaction proceeds. There are also regions where cool flames and ignition occur. These conditions are not suitable for the elucidation of the elementary reaction steps and evaluation of rate constants, as is illustrated by the very limited amount of quantitative information that has been obtained by direct studies of hydrocarbon oxidation despite the large number of investigations that have been made.

Over a number of years, the Hull group has been concerned with devising systems and conditions which permit the evaluation of the elementary steps in hydrocarbon oxidation. Three main approaches have been made.

1. The mechanism of the $H_2 + O_2$ reaction is well established in the temperature range around $500^\circ C$, and rate constants for the reactions involved have been determined accurately. The reaction thus forms a controlled environment in which to study the behaviour of an additive introduced in concentrations sufficiently small to avoid significant disturbance of the radical concentrations. Information can be obtained, first on the rate constants for the reaction of the radicals H and OH with the additive, and secondly on the reactions by which the radical formed from the parent material gives rise to the final products. The advantages of this approach are that the radical environment is under control, that a wide variety of additives can be made to undergo reactions at the same temperature, and that the intermediates believed to be important can be studied individually with the confidence that the radical environment is unaltered.

2. The oxidation of aldehydes in the range $150-300^\circ C$ is a complex process, in which peracids play an important role. At temperatures above $400^\circ C$, however, a much simpler mechanism operates, since the main products, an alkene and carbon monoxide, are much less reactive than the parent aldehyde, so that the complications inherent in the direct oxidation of alkanes do not

occur. The reaction is slightly autocatalytic due to dissociation of the reaction product, hydrogen peroxide, a fortunate situation that permits evaluation of the initiation rate for aldehyde + oxygen, and also enables the rate constant for HO_2 + aldehyde to be determined. The carbonyl radical RCO readily decomposes at these temperatures to R + CO, so that reactions of alkyl radicals can be studied.

3. Because of the strain in the central C-C link, the compounds 2,2,3,3-tetramethylbutane (TMB), and 2,2,3-trimethylbutane (TRIMB), decompose by C-C homolysis at temperatures much lower than most alkanes, and the rate of production of radicals by this process is faster by a factor of 10^2 to 10^3 than by the reaction of the hydrocarbon with oxygen, even at atmospheric pressure of oxygen. The decomposition is thus a source of t-butyl radicals in the case of TMB, and of t-butyl and i-propyl radicals in the case of TRIMB, thus enabling the reactions of these radicals to be studied. In the presence of oxygen, both these radicals react predominantly (99%) to give the HO_2 radical so that a convenient source of this radical over the temperature range 420-560°C is available.

These three approaches are complementary and all can be used to advantage in elucidating the complex processes involved in hydrocarbon oxidation. In many cases, simultaneous use of these methods has prevented wrong conclusions being drawn.

By use of these methods it has been shown that four main types of reaction account for the majority of initial products in alkane oxidation at 450-550°C.

(a) Reaction of the alkyl radical with oxygen to form the conjugate alkene.

(b) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.

(c) Isomerisation of the alkylperoxy radical by internal hydrogen abstraction to form a hydroperoxyalkyl radical, which subsequently decomposes to give oxygenated ring compounds.

(d) Reaction of the hydroperoxyalkyl radical with oxygen to give lower aldehydes and ketones.

A body of rate constants for these four types of reaction is being built up and the patterns involved are beginning to emerge. It should thus be possible to use these patterns to provide rate constants for computer modelling of the initial stages of hydrocarbon oxidation for hydrocarbons which have not been studied experimentally. The possibility has already been examined in the case of n-pentane.

As already pointed out, alkenes are an early product of alkane oxidation, and a full computer modelling of hydrocarbon oxidation requires an understanding of the mechanism of alkene oxidation. This process is even more complex than alkane oxidation, since both radical addition and radical abstraction reactions are possible, and the full range of approaches already described will certainly be needed. Significant progress in understanding the processes involved has been made as a result of detailed studies of the addition of ethene and propene to slowly reacting mixtures of hydrogen and oxygen at about 500°C, and as a result of limited studies with the butenes and pentenes, made incidentally during investigations with the corresponding alkanes. Four main types of reaction appear to account for the main oxidation products from alkenes.

(a) OH addition to the alkene, which appears to be the cause of the high aldehyde yields in alkene oxidation, though the exact mechanism remains uncertain.

(b) HO_2 addition to the alkene, which accounts for the high yields of oxirans.

(c) H addition to form a vibrationally-excited alkyl radical, which then decomposes completely or partially to a lower alkene and a lower alkyl radical.

(d) H-abstraction from the alkene by the radicals H, OH and HO_2 to give an alkenyl radical. Virtually no information is available on the oxidation reactions of these radicals.

Details of individual studies are given in the following pages.

1. The hydrogen + oxygen reaction

Previously published rate constants for the very important elementary steps in the reaction between H_2 and O_2 have been evaluated with increased accuracy by allowing for the effect of self-heating in the system, the reaction of O atoms with hydrogen peroxide, and other minor refinements in the mechanism. The results indicate that, in most cases, the changes in the parameters due to the above effects are less than 10%, and the new values are summarised in Table 1 below.

Table 1

Rate Constant Ratios in $H_2 + O_2$ Reaction at 500°

$k_8/k_2k_{10}^{\frac{1}{2}} = 0.53 \quad (dm^3\ mol^{-1}s^{-1})^{-\frac{1}{2}}$

$k_{8a}/k_2k_{10}^{\frac{1}{2}} = 0.081 \quad (dm^3\ mol^{-1}s^{-1})^{-\frac{1}{2}}$

$k_{11}/k_{10}^{\frac{1}{2}} = 0.0366 \quad (dm^3\ mol^{-1}s^{-1})^{\frac{1}{2}}$

$k_{14}/k_2 = 281$

$k_{14a}/k_2 = 34$

$k_{15}/k_1 = 4.5$

$OH + H_2 = H_2O + H$ (1)

$H + O_2 = OH + O$ (2)

$H + HO_2 = 2OH$ (8)

$H + HO_2 = H_2 + O_2$ (8a)

$HO_2 + HO_2 = H_2O_2 + O_2$ (10)

$HO_2 + H_2 = H_2O_2 + H$ (11)

$H + H_2O_2 = H_2O + OH$ (14)

$H + H_2O_2 = H_2 + HO_2$ (14a)

$OH + H_2O_2 = H_2O + HO_2$ (15)

By use of the accurately known values of k_1, k_2 and k_{10}, and by combining the present results with data at other temperatures, the Arrhenius expressions in Table 2 are recommended. Information in the literature on reactions (14) and (14a) at lower temperatures is conflicting, and the alternative interpretations are discussed in a recently published paper.[1]

Table 2

Recommended Arrhenius Parameters for Reactions in $H_2 + O_2$ System

	$E/\text{kJ mol}^{-1}$	$A/(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$
$H + HO_2 = 2OH$	7.6	5.4×10^{11}
$H + HO_2 = H_2 + O_2$	0	2.8×10^{10}
$H + HO_2 = H_2O + O$	7.6	5.5×10^{10}
$HO_2 + H_2 = H_2O_2 + H$	90.0	2.0×10^{9}
$OH + H_2O_2 = H_2O + HO_2$	4.8	3.7×10^{9}

Studies of the addition of CO to slowly reacting mixtures of $H_2 + O_2$ have enabled values to be obtained for the rate constants for reactions of OH and HO_2 radicals with CO at 500°C. These reactions are of particular interest in the problem of atmospheric chemistry and automobile engine pollution, and conflicting values of k_{22} in particular have been published. Two types of study have been made, first the yields of CO_2 when small amounts ($\ngtr 1\%$) of CO are added, and secondly, the effect of large amounts of CO on the induction period and maximum rate of the slow reaction. Values of $k_{21}/k_1 = 0.235 \pm 0.02$, $k_{22}/k_{10}^{\frac{1}{2}} = 0.42 \pm 0.03$ $(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^{\frac{1}{2}}$ have been obtained at 500°C, which combined with the accurately known values of k_1, k_{10}, give $k_{21} = 0.96 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $k_{22} = 1.9 \times 10^4$. Arrhenius parameters $A_{22} = 5.8 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $E_{22} = 96.0\ \text{kJ mol}^{-1}$ are recommended. This work has been published.[2]

$$OH + CO = CO_2 + H \qquad (21)$$

$$HO_2 + CO = CO_2 + OH \qquad (22)$$

2. Addition of alkanes to slowly reacting mixtures of hydrogen and oxygen

(a) Rate constants for reaction of H atoms and OH radicals with alkanes

Results previously reported[3] for the rate constants for reaction of H atoms and OH radicals with the hydrocarbons ethane, propane, n- and i-butane, and n- and neo-pentane have been re-examined to allow for the pressure changes due to the oxidation of the hydrocarbon, self-heating of the reaction mixture, and removal of the hydrocarbon by attack of O atoms and of HO_2 radicals. A computer treatment has enabled all these complications to be analysed. Although no single factor has a major effect, the combined effect is to reduce the rate constant for OH attack by a factor of approximately 2, whereas the value for H attack is almost unaltered.

$$\begin{array}{lllllll} OH & + & H_2 & = & H_2O & + & H \qquad (1) \\ H & + & O_2 & = & OH & + & O \qquad (2) \\ OH & + & RH & = & H_2O & + & R \qquad (3) \\ H & + & RH & = & H_2 & + & R \qquad (4) \end{array}$$

Examination of the results indicates that the total rate constant for radical attack on an alkane can be obtained by summing the contributions from attack at the three different types of C-H bond, primary, secondary and tertiary, in the molecule. Combination with data by Greiner[4] at lower temperatures for OH attack enables the Arrhenius parameters A_3/A_1 and $(E_1 - E_3)$ to be obtained for each type of bond. The data for C_2-C_5 alkanes are self-consistent, and examination indicates that the overall rate constant ratio k_3/k_1 can be expressed by equation (i).

$$k_3/k_1 = 0.214n_p\exp(1070/T) + 0.173n_s\exp(1820/T) + 0.273n_t\exp(2060/T) \qquad (i)$$

where n_p, n_s and n_t are the number of primary, secondary and tertiary C-H bonds in the molecule. Similar treatment of the data for H atoms gives the expression (ii) for the ratio k_4/k_2 at 480°C.

$$k_4/k_2 = 7.0n_p + 43n_s + 160n_t \qquad (ii)$$

Absolute values of k_3 and k_4 can be obtained by substituting the known values of k_1 and k_2 in expressions (i) and (ii). By fitting a slight curve to the points obtained by Greiner,[5] by Eberius et al.,[6] and by Westenberg and de Haas,[7] Baldwin and Walker[1] give $k_1 = 1.28 \times 10^5\ T^{1.5}\ \exp(-1480/T)$

dm^3 mol^{-1} s^{-1} over the temperature range 300-900 K. The best value of k_2 at 480°C is obtained by combining the ratio $k_4/k_2 = 44$ for ethane from addition studies with Camilleri, Marshall and Purnell's expression[8] $k_4 = 1.32 \times 10^{11} \exp(-4715/T)$, giving $k_2 = 5.7 \times 10^6$ dm^3 mol^{-1} s^{-1}. Data on rate constants at other temperatures are more limited for H than for OH, but on the basis of the data available, the following Arrhenius parameters are recommended.

Table 3

Arrhenius Parameters for H Abstraction by H Atoms from Alkane

Type of bond	E_4/kJ mol^{-1}	A_4 per C-H bond / $dm^3 mol^{-1} s^{-1}$
primary	39.2	2.2×10^{10}
secondary	33.3	4.9×10^{10}
tertiary	25.2	5.1×10^{10}

To deduce the mechanism of product formation in alkane oxidation, it is necessary to know the proportions of the various radicals formed by H and OH attack on the alkane, and equations (i) and (ii) provide the best available method. However, this procedure may be less reliable if there is a high degree of branching in the molecule. This is shown by some experimental studies recently made[9] with 2,2,3,3-tetramethylbutane as additive. The rate constant ratios k_3/k_1 and k_4/k_2 at 480°C are given below for this hydrocarbon and for neopentane and ethane, which also contain only primary C-H bonds.

Table 4

Rate Constant Ratios for H + RH and OH + RH at 480°C

Hydrocarbon	k_3/k_1	k_4/k_2
ethane	5.7 ± 0.5	44 ± 4
neopentane	10.0 ± 1.0	52 ± 5
tetramethylbutane	8.0 ± 1.0	112 ± 8

On a simple additivity basis, these results should each be in the ratio 1:2:3.

Recent work with 2,2,3-trimethylbutane gives $k_3/k_1 = 12.2 \pm 1.5$ and $k_4/k_2 = 257 \pm 10$ at 480°C. These may be compared with values of 17.5 and 265, calculated from expression (i) and (ii). Use of independent data for k_1 and k_2 gives $k_3 = 4.5 \times 10^9$ and $k_4 = 1.48 \times 10^9$ dm^3 mol^{-1} s^{-1}. Combination with Greiner's low temperature results gives $A_3 = (5.9 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1} and $E_3 = 1800 \pm 300$ J mol^{-1}. This work has now been submitted for publication.[10]

The results in Table 4 suggest that the method used to obtain the values for the tertiary C-H bond in equations (i) and (ii) should be slightly refined. The values for k_3^t/k_1, k_4^t/k_2 have thus been obtained from $k_3/k_1 = 12.2$, $k_4/k_2 = 257$ by subtracting the contribution for fifteen primary C-H bonds using the value per primary C-H bond obtained from k_3/k_1, k_4/k_2 for tetramethylbutane. The values of $k_3^t/k_1 = 5.5$, $k_4^t/k_2 = 164$ are in close agreement with values of 5.0, 184 respectively using the values of k_3/k_1, k_4/k_2 for isobutane and allowing for the contribution of primary C-H bonds using the values of k_3/k_1, k_4/k_2 given in Table 4 for neopentane. By combining the present value of k_3^t (calculated from the known value of k_1) obtained from 2,2,3-trimethylbutane and 2,2,3,3-tetramethylbutane with the values given by Greiner,[4] treated in the same way, $\log_{10}(A_3^t/dm^3\ mol^{-1}\ s^{-1}) = 9.23 \pm 0.10$, $E_3^t = -960 \pm 800$ J mol^{-1}. Alternatively, use of the values for isobutane and neopentane gives $\log_{10}(A_3^t/dm^3\ mol^{-1}\ s^{-1}) = 9.41 \pm 0.10$, $E_3^t = 2250 \pm 800$ J mol^{-1}. The reason for the difference in these two sets of parameters, which has its origin in Greiner's results since the two sets of values of k_3^t/k_1 are within 10% at 480°C, is not clear. From the mean line through the log k_3^t, 1/T plots for i-butane and 2,2,3-trimethylbutane, $\log_{10}(A_3^t/dm^3\ mol^{-1}\ s^{-1}) = 9.32 \pm 0.10$, $E_3^t = 460 \pm 950$, and these parameters are recommended for general use with alkanes in the temperature range 300-1500 K.

(b) Reactions of alkyl radicals

The second object of studies of the addition of small amounts of an alkane to slowly reacting mixtures of $H_2 + O_2$ is to obtain information on the reactions of the radicals produced from the alkane, and the mechanism of formation of the various products. The advantages of this approach over direct studies of alkane oxidation have been discussed elsewhere, and include the fact that the radical concentration is controlled by the $H_2 + O_2$ system rather than the alkane, the fact that a wide range of concentrations can be investigated under essentially identical conditions, and that primary and secondary products can easily be distinguished.

Studies with a range of alkanes have clarified considerably the mechanism of oxidation and suggested that the main initial products in alkane oxidation at temperatures around 500°C result from four major types of reaction.

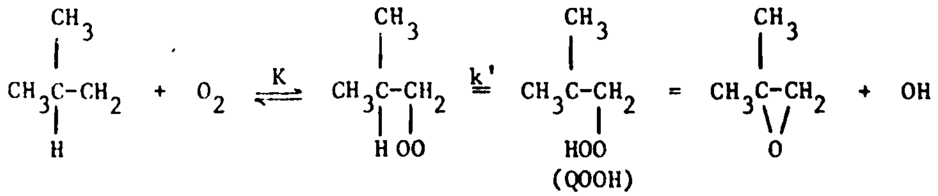
(i) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.

(ii) Formation of conjugate alkenes by the reaction of the alkyl radical with O_2, for example:

$$n\text{-}C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (5p)$$

Although this reaction may occur through addition of O_2 to the alkyl radical to form the RO_2 radical, followed by decomposition to give the alkene + HO_2, this path is kinetically identical to reaction (5p), since R and RO_2 are almost always equilibrated, and the bimolecular form (5p) is preferred.

(iii) Addition of O_2 to form the RO_2 radical followed by isomerisation to give a peroxyalkyl radical (QOOH) and decomposition to give an oxygen-ring compound. This is illustrated by the formation of isobutene oxide from isobutyl radicals.



As shown in previous papers, the overall rate constant for this reaction is given by expression (iii)

$$k = Kk' \qquad (iii)$$

where K is the equilibrium constant for the $R + O_2 = RO_2$ equilibrium.

(iv) Reaction of the peroxyalkyl radical (QOOH) with O_2 to give oxygenated products, such as aldehydes and ketones.

With the completion of studies, now published,[11] with i-butane as additive, rate constants for a number of specific radicals giving specific alkenes have been obtained, and these are summarised in Table 5. The studies with i-butane have been particularly important in two respects. First, a value of $k_5 = 6.8 \times 10^7$ has been obtained which, when combined with a low temperature measurement gives $A_5 = 6.9 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, $E_5 = 29\ kJ\ mol^{-1}$. No other determinations of the Arrhenius parameters for conjugate alkene formation exist. From measurements of the relative yields of isobutene oxide and 3-methyloxetan, a value of $k_6/k_7 = 4.1 \pm 0.4$ is obtained. Use of the rather uncertain value of the rate constant for the decomposition of i-butyl radicals, together with the best thermochemical data available for reaction (8), gives $k_6 = 1.83 \times 10^5\ s^{-1}$, $k_7 = 4.45 \times 10^4\ s^{-1}$ at 480°C. No other experimental value is available for k_6 nor for any similar reaction involving the transfer of a tertiary H atom. Rate constants for the isomerisation of RO_2 radicals to QOOH radicals are summarised in Table 6.

$$CH_3CH(CH_3)CH_2 + O_2 = (CH_3)_2C{=}CH_2 + HO_2 \tag{5}$$

$$CH_3CH(CH_3)CH_2O_2 \rightarrow CH_3C(CH_3)(CH_2OOH) \tag{6}$$

$$CH_3CH(CH_3)CH_2O_2 \rightarrow CH_3CH(CH_2OOH)CH_2 \tag{7}$$

$$CH_3CH(CH_3)CH_2 + O_2 = CH_3CH(CH_3)CH_2O_2 \tag{8}$$

A summary of all the rate constants obtained by the study of i-butane as additive is given in Appendix 1.

A complete analysis of the products when the highly branched alkane 2,2,3,3-tetramethylbutane (TMB) is the additive has been made at 480°C over a wide range of mixture composition. Isobutene in about 95% yield is the only major initial product, although small amounts (ca. 1%) of propene, 2,3,3-trimethylbutene-1, isobutene oxide, formaldehyde and methane are also formed. No evidence has been found for the presence of O-ring compounds containing the same number of carbon atoms as TMB. Thus, even at pressures of O_2 approaching atmospheric, the TMB radical ($(CH_3)_3C\text{-}C(CH_3)_2CH_2$) breaks down almost completely by the dissociation reaction (9) at 480°C. By measuring the yields of (propene + 2,3,3-trimethylbutene-1) relative to i-butene as a function of O_2 concentration, the ratio k_9/k_{10} has been obtained. From a reasonable estimate of k_{10}, based on analogous

Table 5

Rate Constants for Formation of Alkenes and Dienes at 480°C

Radical	Type of CH Bond	Product	$\frac{k}{dm^3 mol^{-1} s^{-1}}$	$k/dm^3 mol^{-1} s^{-1}$ per C-H bond	$\frac{\Delta H}{kJ\ mol^{-1}}$
$C\underline{H}_3CH_2$	Primary	C_2H_4	6.6×10^7	2.2×10^7	-45.0
$C\underline{H}_3CHC\underline{H}_3$	Primary	C_3H_6	1.3×10^8	2.1×10^7	-39.8
$C\underline{H}_3CHCH_2CH_3$	Primary	C_4H_8-1	5.1×10^7	1.7×10^7	-37.5
$CH_3C\underline{H}_2CH_2$	Secondary	C_3H_6	7.1×10^7	3.6×10^7	-53.5
$CH_3CH_2C\underline{H}_2CH_2$	Secondary	C_4H_8-1	1.6×10^8	8.0×10^7	-55.5
$CH_3CHC\underline{H}_2CH_3$	Secondary	C_4H_8-2 (trans)	7.8×10^7	3.9×10^7	-49.0
		C_4H_8-2 (cis)	4.3×10^7	2.2×10^7	-45.0
$(CH_3)_2C\underline{H}CH_2$	Tertiary	i-C_4H_8	6.8×10^7	6.8×10^7	-61.5
$\overline{CH_{\underline{2}}CHCH}CH_2CH_3$	-	$CH_2=CHCH=CHCH_3$	2.1×10^6	1.05×10^6	-14.0

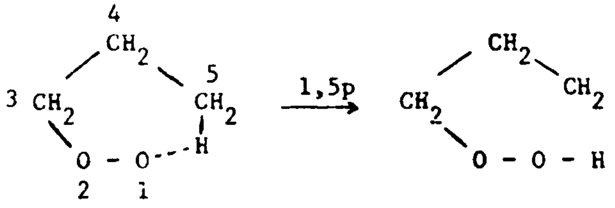
The underlined H atom indicates the site of removal.

Table 6

Rate Constants for the formation of QOOH Radicals

C-H bond broken	Type of H atom transfer[a]	k/s^{-1} at $480^{\circ}C$	E[b]/kJ mol^{-1}
primary	1,3p	(1.3×10^{1})[c]	159
	1,4p	2.2×10^{3}	125
	1,5p	1.8×10^{4}	113
	1,6p	6.0×10^{4}	105
	1,7p	9.3×10^{4}	103
secondary	1,3s	(1.4×10^{2})	144
	1,4s	2.4×10^{4}	111
	1,5s	3.0×10^{5}	95
	1,6s	(6.5×10^{5})	90
tertiary	1,3t	1.5×10^{3}	130
	1,4t	1.8×10^{5}	98
	1,5t	(2.2×10^{5})	84
	1,6t	(7.1×10^{6})	75

[a] In this table, p, s, t refer to abstraction from primary, secondary and tertiary C-H bonds, and the adjacent numbers refer to the position of the atom abstraction as illustrated below for a 1,5p transition.



[b] Calculated using A = $10^{12.1}$ s^{-1}, the value suggested by Benson for a 1,5 transfer. It has been suggested, however, that the value of A decreases as the ring size increases.

[c] Values in brackets are estimates, based on the experimental values.

reactions,* $k_9 = 1.9 \times 10^6\ s^{-1}$ at 480°C. This value is a factor of 10-100 times greater than the values of rate constants for the C-C homolysis of $n\text{-}C_3H_7$, $s\text{-}C_4H_9$, $i\text{-}C_4H_9$ and $neo\text{-}C_5H_{11}$ radicals, presumably because of the considerable strain in the central C-C bond in the TMB radical.

$$(CH_3)_3C\text{-}C(CH_3)_2CH_2 = t\text{-}C_4H_9 + i\text{-}C_4H_8 \tag{9}$$

$$(CH_3)_3C\text{-}C(CH_3)_2CH_2 + O_2 \rightarrow (CH_3)_3C\text{-}C(CH_3){=}CH_2 + HCHO + OH \tag{10}$$

From the yields of 2,3,3-trimethylbutene-1, the rate constant k_{11} has been obtained as $1.1 \times 10^4\ s^{-1}$, close to the expected value for loss of a methyl radical by C-C homolysis. No rate constants for the decomposition processes k_9 and k_{11} were previously available.

$$(CH_3)_3C\text{-}C(CH_3)_2CH_2 = (CH_3)_3C\text{-}C(CH_3){=}CH_2 + CH_3 \tag{11}$$

In the case of propylperoxy, neopentylperoxy and all four species of butylperoxy radical, the hydroperoxyalkyl radicals (QOOH) formed by internal H-atom transfer, either decompose by loss of OH and then cyclise to give an O-ring compound, or add a further molecule of O_2 before decomposing. No evidence has been found for either of these types of reaction in the case of the QOOH radical formed from tetramethylbutylperoxy radicals, and it appears to react uniquely by β- and γ-scission to give lower alkenes, as illustrated by the reaction below.

$$(CH_3)_3C\text{-}C(CH_3)_2(CH_2OOH) \rightarrow i\text{-}C_4H_8 + C_3H_6 + HCHO + OH$$

The shift to C-C scission reactions in the case of QOOH radicals formed from TMB must thus be associated with the steric strain in the central C-C bond.

This work has now been published [9] and the rate constants obtained are summarised in Table 7.

A detailed study[10] has been made over a wide range of mixture composition using 2,2,3-trimethylbutane (TRIMB) as additive; rate constants for H and OH attack on this alkane have been discussed in section (a). The mechanism of product formation is considerably more complex than that for TMB because three different species, A, B, and C, are formed by radical attack on TRIMB.

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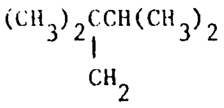
* Reaction (10), though represented kinetically by the equation given, proceeds through formation of the peroxyradical, isomerisation to a peroxyalkyl radical, and subsequent decomposition, as already discussed.

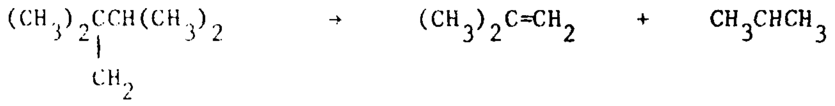


$(CH_3)_2\underset{CH_2}{\underset{|}{C}}CH(CH_3)_2$ $\qquad$ $(CH_3)_3CCH(CH_3)CH_2$ $\qquad$ $(CH_3)_3CC(CH_3)_2$

(A) $\qquad$ (B) $\qquad$ (C)

As a necessary pre-requisite to quantitative interpretation, by using the additivity principle expressed by equations (i) and (ii), the proportions of the three radicals formed may be calculated. For the standard mixture, $O_2 = 70$, $H_2 = 140$, $N_2 = 285$, TRIMB = 5 Torr at 480°C, the initial yields are A = 18.5%, B = 12.5%, and C = 69%, with little change in the proportions as the mixture composition is varied.

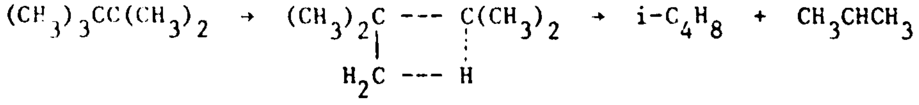
Product analysis shows that the major initial products are isobutene and propene, formed in nearly equal amounts (about 80% of TRIMB consumed for the above mixture), and 2,3,3-trimethylbutene-1 (13%), with lower alkenes, formed by CH_3 loss from radicals A, B, and C, as minor products. The yield of 2,3,3-trimethylbutene-1 increases markedly with increase in the pressure of O_2. It is concluded from a detailed analysis of the results that radicals A and B predominantly undergo homolysis of the strained central C - C bond.



$$(CH_3)_2\underset{CH_2}{\underset{|}{C}}CH(CH_3)_2 \rightarrow (CH_3)_2C{=}CH_2 + CH_3CHCH_3$$

$$(CH_3)_3CCH(CH_3)CH_2 \rightarrow CH_3CH{=}CH_2 + (CH_3)_3C$$

Although previous studies have established that 99% of t-butyl and isopropyl radicals react with O_2 to give isobutene and propene, respectively, under the conditions used, it is clear that radical C must be a major source of these alkenes. After allowance for formation from radicals A and B, the relative rate of formation of isobutene (from C) and 2,3,3-trimethylbutene-1 is inversely proportional to the pressure of O_2. As radical C cannot undergo a simple homolysis of the central C - C bond without H atom transfer, which would be very slow, it is suggested that C decomposes into isobutene and isopropyl radicals in a concerted mechanism.



$$(CH_3)_3CC(CH_3)_2 \rightarrow (CH_3)_2\underset{H_2C}{\underset{|}{C}}\ \text{---}\ \underset{\text{--- H}}{\underset{\vdots}{C}}(CH_3)_2 \rightarrow i\text{-}C_4H_8 + CH_3CHCH_3$$

The oxygen dependence provides strong support for the formation of

2,3,3-trimethylbutene-1 in the following reaction.

$$(CH_3)_3CC(CH_3)_2 \quad + \quad O_2 \quad \rightarrow \quad (CH_3)_3CC(CH_3)=CH_2 \quad + \quad HO_2$$

Rate constants have been obtained for the concerted reaction of radical C and for the various homolyses of radicals A and B, and the values are summarised in Table 7, together with values for the decomposition of related radicals obtained in a similar manner. The values in Table 7 have not previously been determined, and this is indicative of the general lack of rate data for elementary combustion reactions involving alkyl radicals containing more than five carbon atoms.

Measurements at temperatures significantly different from 480°C were not possible, but activation energies may be calculated from estimates of the A factors for the homolyses. From transition state theory, $A = (ekT/h)e^{\Delta S^{\ddagger}/R}$, so that A is effectively determined by the values of $\Delta S^{\ddagger}$. Various arguments may be advanced for a value of $\Delta S^{\ddagger} \sim 4\ J\ K^{-1}\ mol^{-1}$ for all the homolyses, so that A is estimated as $10^{13.8 \pm 0.5}\ s^{-1}$ at 480°C. Combination of this value with the rate constant of each homolysis at 480°C gives the activation energies shown in Table 7, the accuracy specified being due to the uncertainty in the value of A.

A full analysis of the reaction products has also been made with n-pentane as additive. Details of the product distribution have been given in an earlier report and in published papers.[12,13] At the time of the study, no specific rate constants, except for H and OH attack on pentane, were available for any of the elementary reactions involved in the system. However, by use (without modification) of rate constants obtained from studies with $C_2 - C_4$ alkanes and neopentane, it is possible to predict the initial yields of the major products (accounting for 95% consumed) from pentane to better than a factor of 2 over a wide range of mixture composition. The possibility, applied here, of the general use of rate constants determined for specific reactions is of great importance to computer modelling of complex systems, where it is extremely unlikely that a major proportion of the rate constants is known accurately.

Although showing only minor changes from those used above, accurate rate constants for the specific elementary reactions in the pentane system may be obtained from a quantitative treatment of the results. Use of the rate constants for attack of H, OH, and HO_2 at specific C - H bonds in pentane

Table 7

Decomposition of Alkyl Radicals at 480°C

Reaction			ΔU/kJ mol^{-1}	k/s^{-1}	E_f/kJ mol^{-1} (A = $10^{13.8 \pm 0.5}$ s^{-1})
$(CH_3)_3CC(CH_3)_2$	$\rightarrow (CH_3)_2C{=}C(CH_3)_2$	$+ CH_3$	115 ± 4	7.2×10^2	158 ± 7
$(CH_3)_3CCH(CH_3)CH_2$	$\rightarrow (CH_3)_3CCH{=}CH_2$	$+ CH_3$	84 ± 4	6.2×10^4	130 ± 7
$(CH_3)_3CCH(CH_3)CH_2$	$\rightarrow t\text{-}C_4H_9$	$+ C_3H_6$	51 ± 4	1.3×10^6	111 ± 7
$(CH_3)_2C(CH_2)CH(CH_3)_2$	$\rightarrow CH_2{=}C(CH_3)CH(CH_3)_2$	$+ CH_3$	77 ± 4	2.4×10^5	121 ± 7
$(CH_3)_2C(CH_2)CH(CH_3)_2$	$\rightarrow i\text{-}C_3H_7$	$+ (CH_3)_2C{=}CH_2$	59 ± 4	2.4×10^6	107 ± 7
$(CH_3)_3CC(CH_3)_2$*	$\rightarrow i\text{-}C_3H_7$	$+ (CH_3)_2C{=}CH_2$	92 ± 4	7.4×10^5	114 ± 7
$(CH_3)_3CC(CH_3)_2CH_2$	$\rightarrow t\text{-}C_4H_9$	$+ (CH_3)_2C{=}CH_2$	36 ± 4	1.9×10^6	108 ± 7
$(CH_3)_3CC(CH_3)_2CH_2$	$\rightarrow (CH_3)_3CC(CH_3){=}CH_2$	$+ CH_3$	70 ± 4	1.1×10^4	140 ± 7
$CH_3CH_2CHCH_2CH_3$	$\rightarrow CH_3CH_2CH{=}CH_2$	$+ CH_3$	100 ± 4	1.6×10^5	124 ± 7
$CH_3CHCH_2CH_2CH_3$	$\rightarrow C_3H_6$	$+ C_2H_5$	92 ± 4	2.3×10^5	122 ± 7

* A concerted mechanism involving an H atom transfer is suggested for this reaction (see text)

enables the proportions of 1-pentyl, 2-pentyl, and 3-pentyl radicals to be calculated for all the mixtures used. By use of a wide range of H_2, and particularly, of O_2 (8 - 355 Torr) pressures it is possible to confirm suggested mechanisms for the oxidation of each of the three species of pentyl radical. Rate constants have been obtained for the first time for a large number of the elementary reactions involved, and the values form a very consistent pattern with those determined from studies with the C_2 - C_4 alkanes and neopentane as additive. Rate constants for the pentane system are summarised in Appendix II.

3. Addition of alkenes to slowly reacting mixtures of hydrogen and oxygen

Previous studies of the addition of alkanes to slowly reacting mixtures of $H_2 + O_2$ have shown that conjugate and lower alkenes are the major primary products, sometimes in yields of over 80%, in the oxidation of C_2-C_5 alkanes over the temperature range 400-500°C. A full computer modelling of the oxidation process for alkanes thus requires an understanding of the mechanism of alkene oxidation. This oxidation is more complex than the initial stages of alkane oxidation since radical addition to the alkene may occur as well as hydrogen abstraction by the radical. It is not surprising, therefore, that very few rate constants are available for the elementary processes involved. A number of different approaches will be required if the elementary reaction steps are to be disentangled. One such approach involves the addition of small amounts of alkenes to slowly reacting mixtures of $H_2 + O_2$. As with alkane addition, two types of measurement can be made. Study of the loss of hydrocarbon at very low concentrations of additive provides information on radical attack of the alkene, whereas examination of the reaction products (for which a higher concentration of alkene is necessary to provide reasonable yields of products) gives information on the reactions of the radical produced by the primary attack.

(a) Addition of ethene

Results on the addition of C_2H_4 to slowly reacting mixtures of $H_2 + O_2 + N_2$ at 500°C have been re-examined. Two types of measurement have been made.

(1) The pressure change ΔP_{50} corresponding to 50% loss of C_2H_4. Although small corrections are necessary for removal of C_2H_4 by reaction with O atoms, and by reaction with HO_2 in a H-abstraction reaction, the predominant reactions removing C_2H_4 are H and OH abstraction, and H, OH and HO_2 addition. The variation of ΔP_{50} with mixture composition over a wide range provides information on these reactions, though additional information is required if rate constants for all five reactions are to be evaluated.

(2) The yield of products in the early stages of reaction using three mixtures of considerably different $[H_2]/[O_2]$ ratios as indicated below.

Mixture	H_2	O_2	N_2	C_2H_4
		Torr		
I	140	70	285	5
II	140	355	0	5
III	425	70	0	5

The main initial products, and their suggested mode of formation, are indicated below.

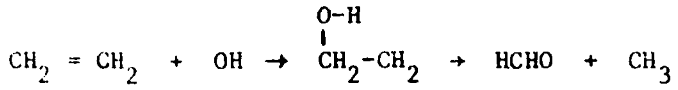
(i) Ethylene oxide (C_2H_4O) is formed almost entirely by addition of HO_2 radicals to C_2H_4.

$$C_2H_4 + HO_2 \rightarrow C_2H_4O + OH \qquad (4)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (5)$$

With the rate constants for H and OH addition and abstraction adjusted to give the best interpretation of the variation of ΔP_{50}, the yields of C_2H_4O (32-40%) require the ratio $k_4/k_5^{\frac{1}{2}} = 1.13\ (dm^3\ mole^{-1}\ s^{-1})^{\frac{1}{2}}$. With $k_5 = 2 \times 10^9\ dm^3\ mole^{-1}\ s^{-1}$, $k_4 = 5.0 \times 10^4\ dm^3\ mole^{-1}\ s^{-1}$ at 500°C. This value is somewhat higher than the figure of 1.7×10^4 obtained by measuring the yield of C_2H_4O obtained when C_2H_4 is added to slowly reacting mixtures of HCHO + O_2 at 60 Torr total pressure. The difference suggests that k_4 may be pressure dependent, and studies of the reaction using the tetramethylbutane + O_2 system as a source of HO_2 radicals (see later) are in progress.

(ii) Methane is formed by addition of OH radicals to C_2H_4, the CH_3 radicals formed predominantly reacting with H_2 to give CH_4.



$$CH_2 = CH_2 + OH \rightarrow \overset{O-H}{CH_2}-CH_2 \rightarrow HCHO + CH_3 \qquad (6)$$

$$CH_3 + H_2 \rightarrow CH_4 + H \qquad (7)$$

If all CH_3 radicals give CH_4, the computer treatment of this mechanism predicts that the yield of CH_4 (experimentally 12-14%) should be almost the same for mixtures I, II and III, as found experimentally when allowance is made for oxidation of the CH_3 radicals.

(iii) Ethane is formed by H-addition to C_2H_4, to give C_2H_5. The predominant reaction of C_2H_5 will be to reform C_2H_4 by reaction (1), so that no net consumption of C_2H_4 occurs, but a competing reaction (8) is also possible.

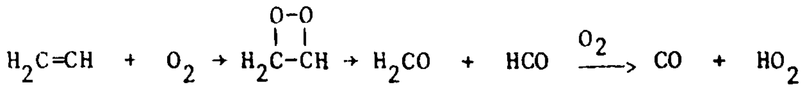
$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad (1)$$
$$C_2H_5 + H_2 \rightarrow C_2H_6 + H \qquad (8)$$

The ratio of the rates of reactions (1) and (8) is $k_1[O_2]/k_8[H_2]$, so that the yield of C_2H_6 should vary markedly with $[H_2]/[O_2]$. This is confirmed experimentally, the initial yields varying from 16% for mixture III to 0.5% for mixture II. From these yields and the known value of k_1/k_8, obtained from earlier studies of the oxidation of C_2H_5CHO in the presence of H_2, the value of the rate constant for addition of H atoms to ethylene can be obtained. Allowance is necessary for the fact that, as indicated by previous studies, this addition proceeds through the reaction sequence given below.

$$\begin{array}{lllll} H + C_2H_4 & \rightarrow & C_2H_5^* & & \\ C_2H_5^* & \rightarrow & C_2H_4 & + & H \\ C_2H_5^* + M & \rightarrow & C_2H_5 & + & M \end{array}$$

(iv) Formaldehyde and Carbon Monoxide. CH_4, C_2H_6 and C_2H_4O account for about 55% of the products for mixture I, 40% for mixture II, 70% for mixture III. The only other primary products are CO and HCHO and although some HCHO is formed in reaction (6) and to a small extent from the CH_3

radicals formed in reaction (6), the main route for formation of both these products is almost certainly from C_2H_3 radicals formed by H-abstraction from C_2H_4.



$$H_2C{=}CH + O_2 \rightarrow H_2\overset{O-O}{\overset{|\quad|}{C-CH}} \rightarrow H_2CO + HCO \xrightarrow{O_2} CO + HO_2$$

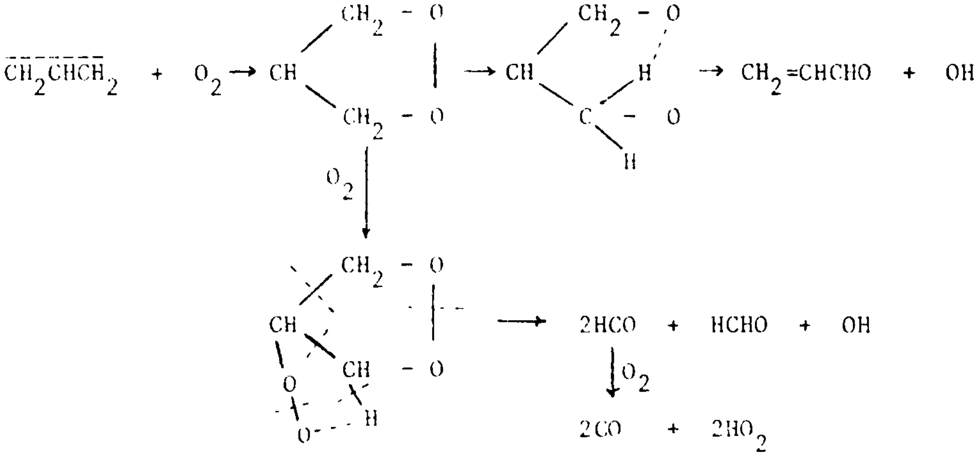
Although the reactivity of HCHO makes determination of its initial yield difficult, the proposed mechanism is supported by the fact that the initial yields of CO and of HCHO (after correction for its formation in reaction (6)) are effectively equal.

Computer treatment of the results obtained with C_2H_4 is in progress to allow a more detailed interpretation and to evaluate rate constants for the reactions involved. In an attempt to reduce the number of unknown rate constants involved, a separate study is being made of the reactions of C_2H_4 with HO_2 radicals, using the tetramethylbutane + O_2 system as a source of these radicals.

Ethylene oxide appears to be a fairly reactive intermediate both in ethane and ethene oxidation, and its role is being examined by studies both of its thermal decomposition and of its oxidation in a radical environment.

(b) Addition of propene

Results obtained by the addition of propene have been re-examined by computer modelling. The formation of the major initial products, ethylene oxide, acetaldehyde, methane, and ethene may be explained by radical addition reactions similar to those discussed in section 3(a) for ethene addition. The products likely to arise from H abstraction (allylic position) from propene, namely acrolein, formaldehyde, and CO represent only about 15-25%, depending on mixture composition, of the propene consumed. A Diels-Alder type of O_2 addition to the allyl radicals is suggested for the formation of these products.



The mechanism is consistent with the observed effect of variation in the pressure of O_2 on the relative yields of acrolein, CO and formaldehyde.

From kinetic studies with propene there is no doubt that the rate constants for abstraction by H and OH (to form the resonance-stabilised allyl radical) are at least a factor of 10 lower than expected on energetic grounds by comparison with those for abstraction from alkanes. This marked fall in the rate constants almost certainly arises mainly from low pre-exponential A factors. Strong kinetic and thermodynamic evidence supports this view. For example, the delocalisation of the pi bond in the transition state of the allyl radical reduces the value of $\Delta S^{\ddagger}$ for H abstraction from propene by about 20 J K^{-1} mol^{-1} compared with that for H + propane. Application of transition state theory then gives an A factor for abstraction from propene about one-tenth of that for abstraction from propane.

(c) Addition of pentene-1 and pentene-2

Results obtained on the addition of pentene-1 and pentene-2 to slowly reacting mixtures of $H_2 + O_2 + N_2$ at 480°C are being interpreted. The initial products can be conveniently divided into four groups according to their mechanism of formation.

(i) By H-abstraction. One difficulty in assessing the importance of these reactions relative to radical-addition reactions is the problem of identifying the products resulting from H-abstraction. With C_2-C_5 alkyl radicals, a reaction of major importance is the formation of the conjugate alkene by a reaction with O_2 involving H atom abstraction from the carbon atom adjacent to the free valency, as for n-C_3H_7 radicals below.

$$CH_3CH_2CH_2 \quad + \quad O_2 \quad = \quad CH_3CH{=}CH_2 \quad + \quad HO_2$$

However, when such abstraction would have to occur from a doubly bound carbon atom, no evidence has been found for the corresponding reaction with alkenyl radicals. Thus no trace of pentadiene-1,2 or pentadiene-2,3 is obtained from pentene-1 or pentene-2. With pentene-1, the resonance-stabilised radical $\overline{CH_2CHCH}CH_2CH_3$ will be formed predominantly by H-abstraction, and the most probable reactions of this radical are either to react with O_2 to give pentadiene-1,3 (yield 15%) or to decompose to give butadiene-1,3 (yield 12%).

$$CH_2{=}CHCH_2CH_2CH_3 \quad + \quad X \rightarrow CH_2CHCHCH_2CH_3 \quad + \quad HX \qquad (9)$$

$$\overline{CH_2CHCH}CH_2CH_3 \quad + \quad O_2 \rightarrow CH_2{=}CH{-}CH{=}CHCH_3 \quad + \quad HO_2 \qquad (10)$$

$$\overline{CH_2CHCH}CH_2CH_3. \quad \rightarrow CH_2{=}CH{-}CH{=}CH_2 \quad + \quad CH_3 \qquad (11)$$

This mechanism would give the ratio [pentadiene-1,3]/[butadiene-1,3] = $k_{10}[O_2]/k_{11}$. The ratio does increase from 1.25 to 5.5 as the pressure of O_2 is increased from 70 Torr (mixture I) to 355 Torr (mixture II). This increase in the ratio is not exactly proportional to $[O_2]$ since some pentadiene-1,3 is formed from the radical $CH_2{=}CH{-}CH_2CH_2CH_2$ which reacts uniquely with O_2 to give about 20% of the total pentadiene-1,3. From a reasonable estimate of k_{11}, k_{10} is obtained as 2.1×10^6 dm^3 mol^{-1} s^{-1} at 480°C. This is the first value of a rate constant for the formation of a conjugated diene by reaction of an alkenyl radical with O_2, and, as Table 5 shows, it is considerably below the values for the analogous reaction of alkyl radicals. However, the alkenes are formed in reactions that are 24 to 48 kJ mol^{-1} more exothermic than reaction (10), and there is a clear trend in Table 5 for the rate constant to increase with increase in exothermicity. A plot of $\log_{10}k$ against ΔH (kJ mol^{-1}) indicates that expression (i) predicts the values of the rate constant k at 480°C to better than a factor of 1.4.

$$\log_{10}k \quad = \quad 5.50 \quad - \quad 0.0411\Delta H \qquad\qquad (i)$$

The values of ΔH for the formation of the non-conjugated pentadiene with adjacent double bonds is about 55 kJ mol^{-1}, and use of equation (i) gives an estimated rate constant of about 2×10^3 dm^3 mol^{-1} s^{-1} at 480°C, which is a factor of 10^3 lower than k_{10}. The absence of pentadiene-1,2 and pentadiene-2,3 in pentene addition is thus to be expected.

(ii) <u>By H-addition</u>

2,4-dimethyloxetan, 2-methyltetrahydrofuran, tetrahydropyran, pentene-2 (from pentene-1) and pentene-1 and trans-pentene-2 (from cis-pentene-2) almost certainly arise solely from pentyl radicals formed by H-addition to the pentenes, and the detailed mechanism has been given in a paper submitted for publication. With propene, the results suggest that nearly all the $n\text{-}C_3H_7$ radicals, formed in a vibrationally excited state by the exothermic addition (ca. 150 kJ mol^{-1}) of H atoms to propene, decompose to C_2H_4 and CH_3. With the butenes, the results suggest that a significant fraction (30-50%) of the excited butyl radicals is stabilised, and then reacts. On addition of cis-pentene-2, the products propene and pentene-1 are only formed from the 2-pentyl radical, by decomposition and by reaction with O_2, respectively.

$$CH_3CHCH_2CH_2CH_3 \rightarrow CH_3CH{=}CH_2 + C_2H_5 \qquad (12)$$

$$CH_3CHCH_2CH_2CH_3 + O_2 \rightarrow CH_2{=}CHCH_2CH_2CH_3 + HO_2 \qquad (13)$$

The initial value of the ratio [propene]/[pentene-1] is 4.0, compared with the calculated value of 3.1 using the rate constants k_{12}, k_{13}, obtained for the 2-pentyl radical produced by H-abstraction from pentane (Mixture I). Similarly, the ratio [trans-pentene-2]/[butene-1] formed from the 3-pentyl radicals is 3.0 when the radical is produced by H-addition to cis-pentene-2, compared to 2.5 when produced from pentane. There is thus little evidence for an enhanced rate of decomposition of the pentyl radicals formed from the pentene by H addition.

$$CH_3CH_2CHCH_2CH_3 \rightarrow CH_3CH_2CH{=}CH_2 + CH_3$$

$$CH_3CH_2CHCH_2CH_3 + O_2 \rightarrow CH_3CH{=}CHCH_2CH_3 + HO_2$$

Examination of the yields of products for pentene-1 addition indicates that the ratio of non-terminal to terminal H-addition, $k_{14nt}/k_{14t} = 0.65 \pm 0.2$.

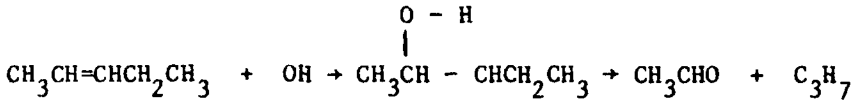
$$H + CH_2{=}CHCH_2CH_2CH_3 \rightarrow CH_2CH_2CH_2CH_2CH_3 \qquad (14nt)$$

$$H + CH_2{=}CHCH_2CH_2CH_3 \rightarrow CH_3CHCH_2CH_2CH_3 \qquad (14t)$$

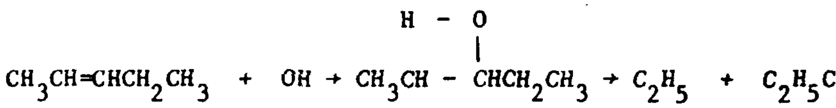
This is much higher than the ratio 0.06 found for C_3H_6 at 298 K and, taken with other evidence, suggests that the discrimination in favour of terminal addition is much reduced as the temperature increases to 500°C.

(iii) By OH addition

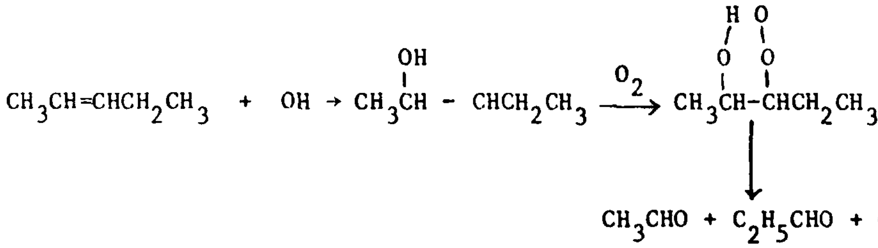
The significant yields of CH_3CHO (10%) and C_2H_5CHO (7%) obtained from pentene-2 almost certainly result from OH addition, either by the single step (15a) or (15b) or by the Waddington mechanism involving the addition of O_2 to the initial adduct as in reaction (16).



$$CH_3CH{=}CHCH_2CH_3 + OH \rightarrow CH_3\overset{O-H}{CH} - CHCH_2CH_3 \rightarrow CH_3CHO + C_3H_7 \qquad (15a)$$



$$CH_3CH{=}CHCH_2CH_3 + OH \rightarrow CH_3CH - \overset{H-O}{C}HCH_2CH_3 \rightarrow C_2H_5 + C_2H_5CHO \qquad (15b)$$

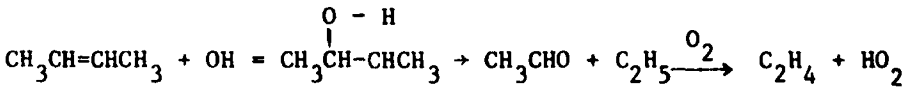


$$CH_3CH{=}CHCH_2CH_3 + OH \rightarrow CH_3\overset{OH}{CH} - CHCH_2CH_3 \xrightarrow{O_2} CH_3\overset{\overset{H\ \ O}{O\ \ \ O}}{CH-CH}CH_2CH_3 \qquad (16)$$

$$\downarrow$$

$$CH_3CHO + C_2H_5CHO + OH$$

In the case of butene-2, the corresponding reaction (15c) would produce C_2H_4, which is not detected as a primary product

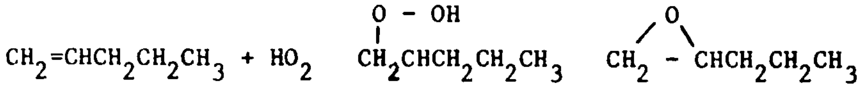


$$CH_3CH{=}CHCH_3 + OH = CH_3\overset{O-H}{CH}-CHCH_3 \rightarrow CH_3CHO + C_2H_5 \xrightarrow{O_2} C_2H_4 + HO_2 \qquad (15c)$$

However, careful analysis of the products suggests that in the case of pentene-2 both mechanisms may be occurring. Further work is thus necessary to establish the relative importance of these two mechanisms.

(iv) By HO_2 addition

The significant yields of 2-propyloxiran (19%) from pentene-1 undoubtedly arise from HO_2 addition, though small amounts will be formed from 1-pentyl and 2-pentyl radicals formed by H-addition to the alkenes.



$$CH_2{=}CHCH_2CH_2CH_3 + HO_2 \quad \overset{O\,-\,OH}{CH_2CH}CH_2CH_2CH_3 \quad \overset{O}{CH_2 - CH}CH_2CH_2CH_3$$

With pentene-2, most of the 2-methyl-3-ethyloxiran appears to come from pentyl radicals, and very little by HO_2 addition. It is planned to measure these rate constants directly by addition of alkenes to the tetramethylbutane + O_2 system discussed later.

4. The oxidation of aldehydes

(a) The oxidation of propionaldehyde

The oxidation of propionaldehyde at 440°C in aged boric-acid-coated vessels[14] has been re-examined with a view to establishing the mechanism of formation of two important products, carbon dioxide and acetaldehyde, which are formed[14] in 5-15% yield, depending on mixture composition.

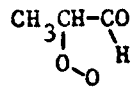
The main products, ethylene, carbon monoxide and hydrogen peroxide are accounted for by the basic mechanism given below.

$$C_2H_5CHO + O_2 = C_2H_5CO + HO_2 \qquad (1)$$
$$C_2H_5CO + M = C_2H_5 + CO + M \qquad (2)$$
$$C_2H_5 + O_2 = C_2H_4 + HO_2 \qquad (3)$$
$$HO_2 + C_2H_5CHO = C_2H_5CO + H_2O_2 \qquad (4)$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (5)$$
$$H_2O_2 + M = 2OH + M \qquad (6)$$
$$OH + C_2H_5CHO = C_2H_5CO + H_2O \qquad (7)$$

The autocatalysis observed in the reaction is attributed[14] to the decomposition of hydrogen peroxide by reaction (6), followed by reaction (7) of the OH radical.

Only a trace of acetaldehyde is formed from C_2H_5 radicals produced by addition of ethane to slowly reacting $H_2 + O_2$ mixtures, so that the reaction $C_2H_5 + O_2 = CH_3CHO + OH$, often used in mechanisms of hydrocarbon oxidation, is not the cause of acetaldehyde formation. It is almost certain that acetaldehyde is formed by radical attack at the secondary CH_2 position, followed by reaction of the radical with O_2.

$$HO_2 + CH_3CH_2CHO = H_2O_2 + CH_3CHCHO \qquad (8)$$



$$CH_3CHCHO + O_2 \rightarrow CH_3CH\text{-}CO \rightarrow CH_3CHO + CO + OH \qquad (9)$$

This sequence is similar to the peroxyradical isomerisation and decomposition (PRID) mechanism given in section (2b).

The ratio $[CO_2]/[CO]$ in the products increases with increase in O_2 concentration, and decreases with increasing addition of inert gas, consistent with a competition between reactions (10) and (2), which gives expression (i) below.

$$d[CO_2]/d[CO] = k_{10}[O_2]/k_2[M] \qquad (i)$$

$$C_2H_5CO + O_2 = C_2H_5CO_3 = C_2H_4 + CO_2 + OH \qquad (10)$$
$$C_2H_5CO + M = C_2H_5 + CO + M \qquad (2)$$

Detailed studies of the variation of $[CO_2]/[CO]$ ratio were made over a wide range of mixture composition, since the system appeared to offer a method of studying the interesting problem of the relative efficiency of different molecules in reaction (2). However, the ratio $[CO_2]/[CO]$ was found to decrease sharply in the early stages of reaction, to an approximately constant value, and then to rise slowly after about 50% consumption of propionaldehyde. This decrease in the ratio was attributed to the simultaneous occurrence of a surface process forming carbon dioxide, which becomes less important as the chain reaction accelerates. The rise in the later stages of reaction is attributed to the oxidation of carbon monoxide by the radicals OH and HO_2, and computer treatment confirms the importance of these reactions in the later stages. Confirmation of the existence of a surface formation of carbon dioxide is provided by the increased $[CO_2]/[CO]$ ratio in smaller diameter vessels, whereas the rate of formation of carbon monoxide is unaffected.

A detailed interpretation of the results for a wide range of mixture composition gives the rate constants at 440°C listed in Table 8.

Table 8

Rate Constants at 440°C in Propionaldehyde Oxidation

$k_1 = 0.077\ dm^3\ mol^{-1}\ s^{-1}$

$k_4 = 1.59 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$

$k_8 = 1.1 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$

$k_{10}/k_2 = 0.108\ (M = N_2)$

The value of k_4 is significantly higher, by a factor of about 4, than preliminary estimates for the rate constant of HO_2 with the secondary CH_2 group in propane, and this suggests that the secondary CH bond is weaker in propionaldehyde than in propane by about 8 kJ mol^{-1} because of the adjacent aldehydic group.

This work has been published.[15]

(b) The oxidation of isobutyraldehyde at 440°C

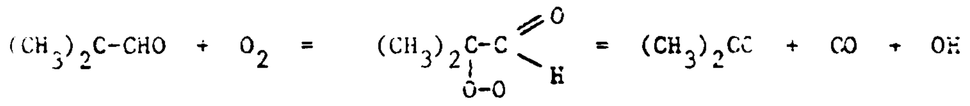
The major products are propene, carbon monoxide and hydrogen peroxide, although small amounts of carbon dioxide (4%), propene oxide (1%), and acetone (in yields of 6-12% depending on mixture composition) are also found. The following scheme accounts for the main reaction products.

$$
\begin{array}{lclclclr}
i\text{-}C_3H_7CHO & + & O_2 & = & i\text{-}C_3H_7CO & + & HO_2 & (1b) \\
i\text{-}C_3H_7CO & + & M & = & i\text{-}C_3H_7 & + & CO + M & (2b) \\
i\text{-}C_3H_7 & + & O_2 & = & C_3H_6 & + & HO_2 & (3b) \\
HO_2 & + & i\text{-}C_3H_7CHO & = & i\text{-}C_3H_7CO & + & H_2O_2 & (4b) \\
 & & 2HO_2 & = & H_2O_2 & + & O_2 & (5) \\
H_2O_2 & + & M & = & 2OH & + & M & (6) \\
OH & + & i\text{-}C_3H_7CHO & = & i\text{-}C_3H_7CO & + & H_2O & (7b)
\end{array}
$$

The formation of acetone is attributed to reactions (4t), (7t) and (11) below. The increase in the percentage yield of acetone as the reaction proceeds may be used to obtain both k_{4t} and k_{7t}, since the rise in acetone yield is due to the increase in the concentration of the less selective OH radical, as a result of an increasing contribution from the dissociation of the product hydrogen peroxide (reaction 6). The increase in acetone concentration with increasing O_2 concentration is attributed to competition between reactions (11) and (12).

$$
\begin{array}{lclclclr}
HO_2 & + & (CH_3)_2CHCHO & = & (CH_3)_2C\text{-}CHO & + & H_2O_2 & (4t) \\
OH & + & (CH_3)_2CHCHO & = & (CH_3)_2C\text{-}CHO & + & H_2O & (7t) \\
(CH_3)_2CCHO & + & O_2 & = & (CH_3)_2CO & + & CO + OH & (11) \\
(CH_3)_2CCHO & + & M & = & C_3H_6 & + & CHO + M & (12) \\
HCO & + & O_2 & = & CO & + & HO_2 & (13)
\end{array}
$$

Although the formation of acetone can be represented kinetically by reaction (11), it is undoubtedly formed by a peroxyradical isomerisation and decomposition (PRID) mechanism analogous to that responsible for the formation of acetaldehyde from propionaldehyde.

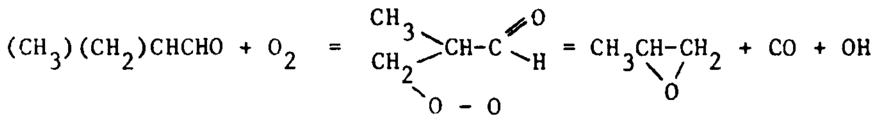


$$(CH_3)_2C\text{-}CHO + O_2 = (CH_3)_2\underset{\substack{|\\O\text{-}O}}{C}\text{-}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H} = (CH_3)_2CO + CO + OH$$

The full mechanism has been treated by a computer program using a Kutta-Runge integration process to examine the variation of the extent of reaction with time, which gives the rate constants $k_{1b} = 0.12 \pm 0.01$ dm^3 mol^{-1} s^{-1}, $k_{4b} = (1.8 \pm 0.1) \times 10^6$ dm^{3}mol^{-1}s^{-1} at 440°C. From the yields of acetone, the values $k_{4t} = (1.4 \pm 0.2) \times 10^5$ dm^3 mol^{-1} s^{-1}, $k_{7t}/k_{7b} = 0.7 \pm 0.1$, $k_{12}/k_{11} = 0.014 \pm 0.002$ ($M = N_2$) have been obtained. The value of k_{4t} is significantly higher than an upper limit of 4×10^4 found for HO_2 attack at the tertiary C-H bond in butane. This confirms the suggestion made in section (3a) that C-H bonds adjacent to an aldehydic group are noticeably weaker than the corresponding bond in an alkane.

Propene oxide is formed both from i-C_3H_7 radicals by reaction (14) and from the radicals formed by OH and HO_2 attack at the primary CH bonds.

$$\text{i-}C_3H_7 + O_2 = C_3H_6O + OH \qquad (14)$$



$$(CH_3)(CH_2)CHCHO + O_2 = \underset{\text{O}-\text{O}}{\overset{CH_3}{CH_2}}\!>\!CH\text{-}C\!\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix} = CH_3CH\text{-}CH_2\ (\text{-O-}) + CO + OH \qquad (15)$$

Allowance for the relatively small amount of propene oxide formed by reaction (15) is included in the computer treatment, which gives the best value of k_{14}/k_{3b} as 0.007. This is consistent with a value for 0.010 for the corresponding ratio for t-C_4H_9 radicals.

As found with propionaldehyde, the $[CO_2]/[CO]$ ratio falls sharply as the reaction proceeds, and then rises later due to secondary formation of carbon dioxide from carbon monoxide. This fall has been interpreted in terms of a heterogeneous formation of carbon dioxide in parallel with a homogeneous formation by isomerisation and decomposition of the $(CH_3)_2CHCO_3$ radical. However, the yield of carbon dioxide is much lower than in the case of propionaldehyde, and varies rather erratically, so that a detailed study of the mechanism of formation is not considered worthwhile.

This work has been published.[16]

(c) Summary of rate constants

Rate constants for the initiation reaction (1) and for the reaction (4) of HO_2 radicals with aldehydes are summarised below.

Table 9

Rate Constants in Aldehyde Oxidation

Aldehyde	k_1 $dm^3 mol^{-1} s^{-1}$	Position of HO_2 attack	k_4 $dm^3 mol^{-1} s^{-1}$	Temp. ^oC
HCHO	0.022	aldehydic	$(5.6 \pm 0.5) \times 10^5$	440
C_2H_5CHO	0.081	aldehydic	$(1.52 \pm 0.15) \times 10^6$	440
		secondary CH_2	$(1.5 \pm 0.2) \times 10^5$	440
$n-C_3H_7CHO$		total	$(2.4 \pm 0.5) \times 10^6$	450
$i-C_3H_7CHO$	0.120	aldehydic	$(1.83 \pm 0.1) \times 10^6$	440
		tertiary	$(1.4 \pm 0.2) \times 10^5$	440

As formaldehyde has two aldehydic C-H bonds, the much lower values both for k_1 and k_4 imply that the activation energy is 8-12 kJ mol^{-1} higher for reactions of HO_2 and of O_2 with formaldehyde compared with higher aldehydes, and a similar difference probably applies to the aldehyde C-H bond dissociation energies.

A paper[17] summarising these results and other rate constants for reactions of HO_2 radicals was presented at the Seventeenth International Combustion Symposium at Leeds in August 1978.

5. The oxidation of 2,2,3,3-tetramethylbutane

(a) The oxidation in KCl-coated vessels

Because of the considerable strain caused by the six CH_3 groups around the central C-C bond, the decomposition of 2,2,3,3-tetramethylbutane (TMB) occurs at temperatures 100-150°C lower than needed for straight chain alkanes. The thermolysis of a hydrocarbon is normally a chain reaction, sensitive to surface effects, but these difficulties can be avoided in the case of TMB by carrying out the decomposition in the presence of O_2. Previous studies have shown that 99% of $t\text{-}C_4H_9$ radicals react with O_2 to form isobutene according to reaction (2). If the reaction is carried out in a KCl-coated vessel, known to be effective for the destruction of HO_2 radicals, the basic mechanism thus involves reactions (1)-(3).

$$(CH_3)_3C\text{-}C(CH_3)_3 = 2t\text{-}C_4H_9 \qquad (1)$$

$$t\text{-}C_4H_9 + O_2 = i\text{-}C_4H_8 + HO_2 \qquad (2)$$

$$HO_2 \overset{\text{surface}}{=} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \qquad (3)$$

This mechanism gives the stoichiometric equation (s) and the relationships (i) and (ii), which have been confirmed experimentally.

$$(CH_3)_3C\text{-}C(CH_3)_3 + \tfrac{1}{2}O_2 = 2i\text{-}C_4H_8 + H_2O \qquad (s)$$

$$\Delta P = 1.5\Delta[\mathrm{TMB}] = 0.75[i\text{-}C_4H_8] \qquad (i)$$

$$-d[\mathrm{TMB}]/dt = k_1[\mathrm{TMB}]^1[O_2]^0 \qquad (ii)$$

However, the experimental rate constant k_{obs}, based on expression (ii), increases slightly (ca.10-20%) with TMB concentration over the range 0.25-4 Torr, and with addition of inert gas. This is attributed to a slight contribution from attack of OH and HO_2 radicals on TMB as the result of the additional reactions (4)-(9) below.

$$HO_2 + \mathrm{TMB} = (CH_3)_3C\text{-}C(CH_3)_2CH_2 + H_2O_2 \qquad (4)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (5)$$

$$H_2O_2 + M = 2OH + M \qquad (6)$$

$$H_2O_2 \overset{\text{surface}}{=} H_2O + \tfrac{1}{2}O_2 \qquad (7)$$

$$OH + \mathrm{TMB} = (CH_3)_3C\text{-}C(CH_3)_2CH_2 + H_2O \qquad (8)$$

$$(CH_3)_3C\text{-}C(CH_3)_2CH_2 = i\text{-}C_4H_8 + t\text{-}C_4H_9 \qquad (9)$$

Studies[9] of the addition of TMB to the $H_2 + O_2$ reaction, discussed in section (have shown that reaction (9) is the predominant reaction of the TMB radical.

Use of a computer program, based on a stationary state treatment of the radical concentrations and a Runge-Kutta integration of the differential equations for the molecular species, has allowed the evaluation of the rate constants k_1 and $k_4/k_5^{1/2}$ from studies over a range of TMB concentration and total pressure. The chain contribution from reactions (4) and (8) is only about 15% of the total reaction rate and is almost independent of temperature between 420-540°C.

The corrected values of k_{obs} give a good straight line plot of $\log k_1$ against 1/T over the range 420-540°C, with Arrhenius parameters $A_1 = 1.2 \times 10^{17}\ s^{-1}$, $E_1 = 295.4 \pm 1.5$ kJ mol^{-1}, which may be compared with $A_1 = 2 \times 10^{16}\ s^{-1}$, $E_1 = 286.5$ kJ mol^{-1} over the range 713-868°C, obtained by Tsang[18] using a shock tube. Combination of Tsang's data, suitably corrected, with the present data gives $A_1 = 6.0 \times 10^{16}\ s^{-1}$, $E_1 = 290.4 \pm 1.5$ kJ mol^{-1} over the range 420-868°C. Combination of the value of E_1 with that for the reverse reaction and with other thermodynamic data gives the enthalpy of formation $\Delta_f H^o_{298} = 44.0 \pm 4.0$ kJ mol^{-1} for the t-C_4H_9 radical, which is at least 10 kJ mol^{-1} higher than previously accepted values. The value of $\Delta_f H^o_{298}$ leads to a bond dissociation energy D^o_{298}(t-Bu-H) = 396.6 kJ mol^{-1}, *which again is significantly* higher than the previously accepted value of 382 kJ mol^{-1}. Recommended values for the bond dissociation energies in the C_1-C_4 alkanes are given later.

This work has been published.[19]

(b) The reaction of HO_2 radicals with 2,2,3,3-tetramethylbutane

The increase in the observed value of the rate constant k_{obs}, obtained from expression (i), with increase in TMB concentration and on addition of inert gas is due to a small chain contribution (chain length less than unity) from reactions (4) and (8). At the lower temperatures (420 and 440°C) this is predominantly due to reaction (4), but as the temperature rises, the increased dissociation of H_2O_2 causes an increasing contribution from reaction (8); at the same time the contribution from HO_2 attack decreases because reaction (5) becomes increasingly dominant as the concentration of radicals increases. Computer interpretation of the mechanism involving reactions (1)-(9) gives a preliminary value of $k_4 = 1.7 \times 10^4$ at 440°C. However, although the individual values of the surface termination constant k_3 and the homogeneous termination constant k_5 are known, the total termination rate is not the sum of the two individual termination rates because of interaction between the homogeneous termination, which gives a uniform concentration of radicals across the reaction vessel, and the surface destruction, which gives a diffusion-controlled profile. The occurrence of homogeneous termination increases the concentration gradient near the vessel surface, so that the rate of surface termination is greater than when homogeneous termination is absent. There has been no previous study of the extent of this interaction. Calculations with linear homogeneous termination, where the differential equations can be integrated, shows that the total termination rate may be increased by as much as 20%. Since this means that the concentration of HO_2 radicals may be about 20% below that calculated using conventional treatments, appreciation of this interaction is essential if accurate rate constants are to be obtained using the oxidation of TMB in KCl-coated vessels as a source of HO_2 radicals.

With mutual termination, there is no explicit solution of the simultaneous differential equations involved and numerical methods of solution have to be adopted. In collaboration with the Department of Applied Mathematics, a suitable program has been written to solve the second order differential equation in the case where chain initiation results only from the decomposition of TMB. Since the concentration of TMB is uniform across the reaction vessel, the rate of initiation is also uniform. Solution of the problem using the computer program requires an intelligent guess as to the radical concentration at the centre of the vessel, and experience has enabled this to be achieved. The results show that again the total termination rate may be some 20% higher than if interaction is ignored.

However, the real situation is more complex since H_2O_2 can dissociate by reaction (6) and thus also produce chain centres. Moreover, since H_2O_2 is produced from HO_2, its concentration is not uniform across the vessel, and its diffusion to the surface has also to be considered. This creates a pair of simultaneous differential equations which have to be numerically integrated, and to obtain a solution, starting values of the concentrations of HO_2 and H_2O_2 at the centre of the vessel have to be provided. If the guesses are not sufficiently accurate, the program finds erroneous solutions. This difficulty, arising from the stiffness of the equations, has slowed down progress, particularly at the higher temperatures when assessment of the starting values is more critical.

From the results so far obtained for the extent of interaction, the observations at 440°C have been re-examined. The value of k_1 is effectively unaltered, but the revised value of k_4 is 2.07×10^4 $dm^3 mol^{-1} s^{-1}$. The increase of about 20% on the previous figure is entirely due to the interaction phenomena. With an accurate value for k_4 now available, the TMB oxidation can now be used as a source of HO_2 radicals so as to obtain rate constants for HO_2 + some additive.

This value for k_4 represents the first direct determination of a rate constant for the HO_2 radical with an alkane. The uncorrected value was reported[17] at the Seventeenth International Combustion Symposium at Leeds in 1978.

(c) The molecular decomposition of 2,2,3,3-tetramethylbutane

A small amount (ca. 1%) of i-butane is found in the decomposition of TMB in the presence of O_2. The rate of production of i-butane is first order in TMB, and is independent of the concentration of O_2, of inert gas addition, and of vessel diameter. These observations leave as the only possibility a molecular mechanism for i-butane formation.

$$(CH_3)_3C\text{-}C(CH_3)_3 \quad = \quad i\text{-}C_4H_{10} \quad + \quad i\text{-}C_4H_8 \qquad (1M)$$

Study of the molecular decompositions between 420-540°C gives the Arrhenius parameters $A_{1M} = 7.8 \times 10^{13}\ s^{-1}$, $E_{1M} = 275 \pm 1.5$ kJ mol^{-1}. The A factor is consistent with that expected for a four-centre transition state. These parameters appear to be the first reported for the non-chain, molecular decomposition of an alkane. This work has been published.[20]

(d) Reaction of C_2H_5 radicals with O_2

In a previous report, the rate constant for reactions of HO_2 radicals with C_2H_6 was determined by measuring the relative yields of isobutene and C_2H_4 formed when C_2H_6 is added to TMB + O_2 mixtures. With the simplest mechanism involving reactions (1)-(3), (10) and (11), the relative yields are given by equation (iii)

$$HO_2 + C_2H_6 \rightarrow C_2H_5 + H_2O_2 \qquad (10)$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad (11)$$

$$d[C_2H_4]/d[i\text{-}C_4H_8] \rightarrow k_{10}[C_2H_6]/k_3 \qquad (iii)$$

In an accurate evaluation of k_{10}, allowance must be made for the occurrence of reactions (4)-(9), as well as reaction (12), and detailed computer interpretation is in progress.

$$OH + C_2H_6 \rightarrow C_2H_5 + H_2O \qquad (12)$$

Although the predominant product formed from C_2H_6 is C_2H_4, a trace of ethylene oxide (C_2H_4O) is formed and the ratio $[C_2H_4]/[C_2H_4O]$ can be accurately measured as a result of the increased sensitivity and reproducibility possible with a recently acquired Perkin-Elmer Sigma I gas chromatograph. It is found that at small extents of reaction, the ratio $[C_2H_4]/[C_2H_4O]$ is constant at 95 at 500°C, but that the ratio decreases as the reaction proceeds, almost certainly because of reaction (13).

$$C_2H_4 + HO_2 \rightarrow C_2H_4O + OH \qquad (13)$$

Since the initial ratio $[C_2H_4]/[C_2H_4O] = k_{11}/k_{14}$, the variation of the initial ratio with temperature over the range 400-540°C has been used to obtain the Arrhenius parameter $A_{11}/A_{14} = 13.6 \pm 2.1$, $E_{14} - E_{11} = 12.5 \pm 1.0$ kJ mol^{-1}.

$$C_2H_5 + O_2 \rightarrow C_2H_4O + OH \qquad (14)$$

From measurements of the trace amounts of butane formed by reaction (15), the concentration of C_2H_5 radicals can be calculated from the known value of k_{15}.

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \qquad (15)$$

Since $d[C_2H_4]/dt = k_{11}[C_2H_5][O_2]$, the measurement of the rate of formation of C_2H_4 can be used to obtain $k_{11} = 7.7 \times 10^7$ dm^3 mol^{-1} s^{-1} at 540°C. Combination of this value with an independent estimate at 440°C gives $A_{11} = 10^{8.93}$ dm^3 mol^{-1} s^{-1}, $E_{11} = 16.2$ kJ mol^{-1}, which are considered to be the most reliable parameters available for this reaction.

From these parameters for A_{11}, E_{11}, values of $A_{14} = 6.3 \times 10^7$ dm^3 mol^{-1} s^{-1} $E_{14} = 28.7$ kJ mol^{-1} are obtained. However, the overall reaction (14) is considered to proceed by a peroxy radical isomerisation and decomposition process, represented by equations (16)-(18).

$$\dot{C}_2H_5 + O_2 \rightleftharpoons C_2H_5O_2 \qquad (16)$$

$$C_2H_5O_2 \rightarrow C_2H_4OOH \qquad (17)$$

$$C_2H_4OOH \rightarrow C_2H_4O + OH \qquad (18)$$

On the assumption that (18) is the sole reaction of C_2H_4OOH radicals, and that reaction (16) is effectively equilibrated, the rate constant $k_{14} = K_{16}k_{17}$. Using Benson's additivity rules to evaluate K_{16}, the experimental values of A_{14}, E_{14} given above lead to $A_{17} = 10^{13.29}$ s^{-1}, $E_{17} = 144.0 \pm 10$ kJ $mole^{-1}$. The values are the first experimental determinations of the Arrhenius factors for such reactions. This value of A_{17} is a factor of ten higher than the figure suggested by Benson for similar isomerisations of alkylperoxy radicals to the hydroperoxyalkyl radical which give oxetans on decomposition. Since these involve a 6-membered ring in the transition state, compared to a 5-membered ring of reaction (17), this is consistent with transition state theory which indicates that the A factor for such isomerisation reactions should increase significantly as the ring size decreases.

This work has been accepted for publication.

(e) Reactions of t-butyl radicals

The basic mechanism involving reactions (1)-(3) indicates that the decomposition of TMB in the presence of O_2 offers a controlled source of t-butyl radicals. If H_2 is added, $i\text{-}C_4H_{10}$ is formed by reaction (19), and the competition between reactions (2) and (19) gives expression (iv).

$$t\text{-}C_4H_9 + O_2 = i\text{-}C_4H_8 + HO_2 \qquad (2)$$

$$t\text{-}C_4H_9 + H_2 = i\text{-}C_4H_{10} + H \qquad (19)$$

$$d[i\text{-}C_4H_{10}]/d[C_4H_8] = k_{19}[H_2]/k_2[O_2] \qquad (iv)$$

In using equation (iv) allowance must be made for the occurrence of reactions (9) and (1M) in which i-butene is formed but not via the $t\text{-}C_4H_9$ radical, and for reaction (1M) which forms i-butane by a molecular process. Because of the small yields of i-butane, high ratios (100-300) of $[H_2]/[O_2]$ must be used. The ratio $d[i\text{-}C_4H_{10}]/d[i\text{-}C_4H_8]$ is found to be proportional to $[H_2]/[O_2]$ as predicted by equation (iv), and the ratio k_2/k_{19} varies from 11,950 to 3,180 over the temperature range 440-540°C, corresponding to values of $A_2/A_{19} = 0.35 \pm 0.10$, $(E_{19} - E_2) = 61.9 \pm 2.0$ kJ mol^{-1}. Use of the known value of k_{-19} and of thermochemical data for reaction (19) gives the values $A_{19} = 2.30 \times 10^9$ dm^3 mol^{-1} s^{-1}, $E_{19} = 71.0 \pm 6.0$ kJ mol^{-1}, $A_2 = 8.0 \times 10^8$ dm^3 mol^{-1} s^{-1}, $E_2 = 9.1 \pm 10$ kJ mol^{-1}. Although subject to some uncertainty, the low value for E_2 confirms the view that reactions of alkyl radicals with O_2 to give the conjugate alkene have a low activation energy.

The data are mostly self-consistent with a value of $\Delta_f H(t\text{-}C_4H_9)$ = 16.1 kJ at 480°C. This corresponds to a value of $D^o_{298}(t\text{-}C_4H_9)$ of 392.7 kJ mol^{-1}. This value is some 10 kJ mol^{-1} higher than earlier estimates by other workers, but is consistent with values recommended for other alkyl radicals which are listed in section 6.

This work has been published.[21]

(f) Reactions of HO_2 radicals with alkanes, alkenes and carbon monoxide

There is considerable difficulty in finding a suitable source of HO_2 radicals in the temperature range 400-550°C, since with most methods of production of this radical, it is accompanied by more reactive radicals. However, the decomposition of TMB in the presence of O_2 offers a source of HO_2 radicals since, as already indicated, the mechanism is described with reasonable accuracy by reactions (1)-(3) and (5) below.

$$(CH_3)_3C\text{-}C(CH_3)_3 = 2\,t\text{-}C_4H_9$$

$$t\text{-}C_4H_9 + O_2 = i\text{-}C_4H_8 + HO_2 \qquad (2)$$

$$HO_2 \overset{\text{surface}}{=} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \qquad (3)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (5)$$

An added alkane, such as ethane, will be removed by reaction (10), the predominant reaction of the C_2H_5 radicals produced being to form C_2H_4 by reaction (11).

$$HO_2 + C_2H_6 = C_2H_5 + H_2O_2 \qquad (10)$$

$$C_2H_5 + O_2 = HO_2 + C_2H_4 \qquad (11)$$

If HO_2 radicals are predominantly destroyed by reaction (3), the above scheme gives the rate expression (v), whereas if reaction (5) predominates over (3), the rate expression (vi) is obtained.

$$d[C_2H_4]/d[i\text{-}C_4H_8] = k_{10}[C_2H_6]/k_3 \qquad (v)$$

$$d[C_2H_4]/d[i\text{-}C_4H_8] = 0.5k_{10}[C_2H_6]/(k_1k_5[TMB])^{\frac{1}{2}} \qquad (vi)$$

Expression (v) is found to be approximately correct at low temperatures and pressures, where the HO_2 concentration is low, whereas expression (vi) is approached as the temperature and pressure increase. For accurate treatment, allowance must be made for the dissociation of hydrogen peroxide, reaction of HO_2 radicals with TMB, reaction of OH radicals both with ethane and TMB, reactions of C_2H_5 and $t\text{-}C_4H_9$ radicals with O_2 to give products other than the conjugate alkene, formation of i-butene by the molecular reaction (1M) and by the decomposition reaction (9) of the TMB radical. All these effects are allowed for in a suitable computer treatment of the mechanism. Allowance is also made for a small amount of ethylene formed by a surface reaction, this process being most important at low TMB concentrations and low ethane concentrations.

Preliminary interpretation gives a value of $k_{10} = 1.27 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$, but a more precise value has awaited the examination of the interaction between homogeneous and heterogeneous termination, discussed in section (5b), which affect the stationary concentration of HO_2 radicals in the oxidation of TMB. The detailed examination now proceeding suggests a value of k_{10} close to $1.5 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$.

The above studies with ethane have shown that the decomposition of TMB in the presence of O_2 provides a very convenient source of HO_2 radicals and a detailed study of their reactions with a wide range of alkanes and alkenes is planned. Very few rate constants for these reactions are available.

Isobutene is the major initial product (99% yield) when TMB is decomposed in the presence of O_2 in KCl-coated vessels over the temperature range 420-540°C. Later in the reaction, secondary products are formed from isobutene and affect the overall kinetics. Studies have, therefore, been made of the addition of isobutene to slowly reacting mixtures of TMB + O_2 with two major objectives.

(i) A determination of the Arrhenius parameters for the reaction of HO_2 radicals with isobutene.

$$HO_2 + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2\underset{O}{C-CH_2} + OH$$

Very little information is available on the addition reactions of HO_2 radicals with alkenes.

(ii) A general study of the chemistry of isobutene oxidation in the TMB + O_2 system, which will also permit the interpretation of the parent system to be carried out further into reaction than is possible at present.

Analytical studies at 470°C, using a mixture containing 2, 1, 30, and 27 Torr of TMB, isobutene, O_2, and N_2, show that the major initial products are acetone (20% yield), isobutene oxide (20%), propene (15%), methane (11%), 2-methylprop-2-en-1-al (11%), isobutyraldehyde (5%), ethylene (5%), 2-methylbutene-1 (5%), and allene (4%). Analyses are currently being carried out for HCHO, CO, and CO_2. Variation in the mixture composition does not greatly affect the product distribution. The concentration of isobutene oxide reaches a maximum early in the reaction since it is rapidly removed by isomerisation processes; this has been confirmed by direct studies of the isomerisation of isobutene oxide. Plausible mechanisms for the formation of the products can be suggested and from further analysis in the very early stages of reaction, by the use of magnetic valves to obtain precise reaction times, rate constants for several of the important elementary reactions should be determined for the first time.

Studies are also being made with the addition of ethylene, to examine the possibility that the reaction $HO_2 + C_2H_4$ is pressure dependent.

Although the reaction between HO_2 radicals and CO is an important step in various combustion processes, its rate constant and Arrhenius parameters are still uncertain.

$$HO_2 + CO \rightarrow CO_2 + OH \qquad (20)$$

Attempts have been made to study reaction (20) by the addition of CO to mixtures of tetramethylbutane + O_2 in KCl-coated vessels. Although reproducible results can be achieved by careful conditioning of the reaction vessel, it is clear that a significant proportion of the CO_2 is formed at the vessel surface, and thus a reliable rate constant cannot be determined.

Recently, however, aged boric-acid-coated vessels have been used with considerable success and surface effects appear to be absent. Although the radical ratio $[OH]/[HO_2]$ is considerably higher than in the KCl-coated vessels, the formation of CO_2 through the reaction of OH radicals with CO may be accurately calculated and does not exceed about 10% of the total yield. A preliminary value of $k_{20} = 9.6 \times 10^3$ dm^3 mole^{-1} s^{-1} at 470°C has been obtained. The study is currently being extended to cover the temperature range 420-500°C and by combination with independent data, reliable Arrhenius parameters for reaction (20) should be obtained.

(g) The oxidation of 2,2,3,3-tetramethylbutane in boric-acid-coated vessels

Although the efficient destruction of HO_2 radicals and of H_2O_2 at a KCl-coated surface minimises the role of OH radicals produced by the dissociation reaction (6) of H_2O_2, use of this surface has two disadvantages.

$$H_2O_2 \quad + \quad M \quad \rightarrow \quad 2OH \quad + \quad M \qquad (6)$$

(i) As the temperature, and hence the concentration of HO_2, increase, H_2O_2 is formed increasingly by reaction (5) and its dissociation becomes more important. Allowance for this is complicated by the interaction between homogeneous and heterogeneous termination, discussed in section (5b).

(ii) The KCl-coated surface deteriorates with use, so that weekly re-coating is necessary, thus slowing down the experimental work.

As a consequence, the reaction has been re-examined in aged boric-acid-coated vessels, where surface destruction of HO_2 and H_2O_2 is effectively negligible. A detailed study has now been carried out between 400 and 470°C; this range will be extended to at least 500°C by the use of precision solenoid valves for the accurate control of reaction time. Wide variations in the concentrations of O_2, TMB, and total pressure have been used in order to confirm the mechanism and to maximise the information derived from the system.

The reaction is markedly autocatalytic due to the occurrence of reaction (6) and the extent of autocatalysis increases markedly with increase in total pressure. As the H_2O_2 does not rapidly reach a stationary concentration as in KCl-coated vessels, but continues to build up for at least 30% of the reaction, the partial differential equations for reactants and for H_2O_2 have to be solved by numerical integration using a computer treatment.

Computer intepretation confirms that the system is a promising source of HO_2 and of OH radicals. By use of an optimisation procedure, preliminary values of $k_1 = 2.2 \times 10^{-5}\ s^{-1}$, $k_4/k_5^{\frac{1}{2}} = 0.48\ (dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$ at 440°C are obtained, which compare with $k_1 = 2.6 \times 10^{-5}\ s^{-1}$ and $k_4/k_5^{\frac{1}{2}} = 0.48\ (dm^3\ mol^{-1}\ s^{-1})$ for the KCl-coated vessels. At present the sensitivity of the optimised parameters to changes in the other rate constants used in the computer treatment is being examined. When the studies are complete, Arrhenius parameters for reactions (1) and (4) will be obtained, together with a value for the second body coefficient of TMB in reaction (6). This latter value is of particular importance to the successful interpretation of the boric-acid-coated results, and experiments specificially designed for the determination have been carried out.

$$(CH_3)_3CC(CH_3)_3 \rightarrow 2t\text{-}C_4H_9 \tag{1}$$

$$HO_2 + (CH_3)_3CC(CH_3)_3 \rightarrow (CH_3)_3CC(CH_3)_2CH_2 \tag{4}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{5}$$

6. The decomposition of 2,2,3-trimethylbutane in the presence of oxygen

Although the strain in the central C-C bond in 2,2,3-trimethylbutane (TRIMB) is less than in 2,2,3,3-tetramethylbutane (TMB), it is still sufficient for the homolysis of the bond to be reasonably fast at about 500°C. As the t-C_4H_9 and i-C_3H_7 radicals produced predominantly react with O_2 to give the conjugate alkene and HO_2, the following simple scheme forms the basis of the mechanism in KCl-coated vessels where HO_2 radicals are efficiently destroyed at the surface.

$$(CH_3)_3C\text{-}CH(CH_3)_2 \rightarrow t\text{-}C_4H_9 + i\text{-}C_3H_7 \qquad (21)$$

$$t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2 \qquad (2)$$

$$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \qquad (22)$$

$$HO_2 \xrightarrow{\text{surface}} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \qquad (3)$$

This simple mechanism gives the rate expression (vii) exactly analogous to expression (i) obtained with TMB.

$$-d[TRIMB]/dt = k_{21}[TRIMB]^1[O_2]^0 \qquad (vii)$$

Experimentally the rate is found to be zero order in O_2, but the observed rate constant k_{obs} increases with the concentration of TRIMB because of the significant chain contribution from HO_2 and OH attack on TRIMB. By a double extrapolation of the observed rate constant k_{obs} to zero extent of reaction for a given initial concentration of TRIMB and to zero initial concentration of TRIMB, accurate values of k_{21} are obtained at 480°C and 500°C. Combination with Tsang's results at higher temperatures then gives $\log_{10}(A_{21}/s^{-1}) = 16.46 \pm 0.12$ and $E_{21} = 305 \pm 1.5$ kJ mol^{-1} over the temperature range 480°-925°C. Combination of these parameters with those for reaction (- 21) gives further information on the thermochemistry of t-C_4H_9 and i-C_3H_7 radicals, which has been the subject of considerable recent discussion. Table 10 gives the enthalpies of formation of t-C_4H_9 and i-C_3H_7 radicals together with the recommended values for CH_3 and C_2H_5 radicals.

Table 10

Thermochemical values of alkyl radicals

R	$\Delta_f H^o_{298}$/kJ mol^{-1}	D^o_{298}(R-H)/kJ mol^{-1}
CH_3	145.6±1.0	438.4±1.0
C_2H_5	118.0±4.0	420.5±4.0
i-C_3H_7	80.8±4.0	402.5±4.0
t-C_4H_9	37.6±2.0	390.2±2.0

From the variation of k_{obs} with the concentration of TRIMB, a preliminary estimate of k_{23} = (3.1 ± 0.6) x 10^5 dm^3 mol^{-1} s^{-1} at 500°C has been obtained.

$$HO_2 + (CH_3)_3C\text{-}CH(CH_3)_2 \rightarrow (CH_3)_3CC(CH_3)_2 + H_2O_2 \qquad (23)$$

Although i-butene and propene are the major initial products (ca. 80% initial yield), as predicted by the mechanism, 2,3,3-trimethylbut-1-ene is formed in about 15% yield together with smaller amounts of 2,3-dimethylbut-2-ene. From the variation in the relative yields of the two products with mixture composition, it has been established that they are formed in reactions (24) and (25).

$$(CH_3)_3CC(CH_3)_2 + O_2 \rightarrow (CH_3)_3C\text{-}C(CH_3)\text{=}CH_2 + HO_2 \qquad (24)$$

$$(CH_3)_3CC(CH_3)_2 \rightarrow (CH_3)_2C\text{=}C(CH_3)_2 + CH_3 \qquad (25)$$

A value of k_{25} = 1.4 x 10^3 at 500°C has been obtained, which is consistent with the rate constants for other 'strained' alkyl radical decomposition as shown in Table 7.

This work has now been published.[23]

7. The reaction between hydrogen and nitrous oxide

The reaction between hydrogen and nitrous oxide has been studied mass spectrometrically at 500°C in a Pyrex vessel to confirm the mechanism below suggested by a study of the reaction at 600°C, and to obtain the activation energies of some of the reactions involved.

$$\mathrm{N_2O + M = N_2 + O + M} \qquad (1)$$
$$\mathrm{O + H_2 = OH + H} \qquad (2)$$
$$\mathrm{H + N_2O = OH + N_2} \qquad (3)$$
$$\mathrm{OH + H_2 = H_2O + H} \qquad (4)$$
$$\mathrm{H + N_2O = NH + NO} \qquad (7)$$
$$\mathrm{NH + N_2O = HNO + N_2} \qquad (8)$$
$$\mathrm{H + HNO = H_2 + NO} \qquad (9)$$
$$\mathrm{OH + HNO = H_2O + NO} \qquad (10)$$
$$\mathrm{H + NO + M' = HNO + M'} \qquad (11)$$
$$\mathrm{HNO + HNO = H_2O + N_2O} \qquad (12)$$
$$\mathrm{HNO + M' = H + NO + M'} \qquad (13)$$
$$\mathrm{HNO + NO = OH + N_2O} \qquad (14)$$

The behaviour of the reaction at 500°C is very similar to that at 600°C. Nitric oxide is formed as a minor product, reaching a maximum concentration and then decreasing as the reaction proceeds. The self-inhibition characteristics of the reaction are due to the marked retarding effect of nitric oxide on the reaction. Attention has been concentrated on the [NO], time profile for the mixture $[N_2O] = [H_2] = [Ar] = 100$ Torr and on the initial rates of nitrogen formation when small amounts of nitric oxide (0.1-5 Torr) are added to this mixture. This avoids the difficulties caused by uncertain coefficients for H_2 and Ar relative to N_2 as M in reaction (1) when the concentrations of the main reactants are varied.

Use of a computer treatment already developed to interpret the results at 600°C shows that, as at 600°C, several combinations of rate constants will give a satisfactory interpretation of the results. Work is continuing to establish the best combination of rate constants and to use the computer program to examine what experiments might provide further information on this system.

Some studies have been made involving the addition of ethane to slowly reacting mixtures of H_2 + N_2O at 550°C with the intention of using the system as a source of H and OH radicals in the absence of O_2. The major product initially is ethylene, but it rapidly reaches a steady concentration, probably due mainly to the equilibrium (15).

$$H + C_2H_4 = C_2H_5 \tag{15}$$

Once equilibrium has been established, methane becomes the major product and the kinetic features of the reaction suggest that it is produced by reactions (16) and (17).

$$H + C_2H_5 = 2CH_3 \tag{16}$$

$$CH_3 + H_2 = CH_4 + H \tag{17}$$

It was hoped that alkoxy radicals might be produced by reaction (18), so that their behaviour could be investigated, but no evidence for this reaction has been found.

$$C_2H_5 + N_2O = C_2H_5O + N_2 \tag{18}$$

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2. "The reaction of OH radicals and HO_2 radicals with carbon monoxide".
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3. "The mechanism of conjugate alkene formation and the importance of surface reactions in hydrocarbon oxidation".
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4. "Decomposition of 2,2,3,3-tetramethylbutane in the presence of oxygen".
G. M. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker.
J. Chem. Soc., Faraday I, 1978, 74, 366.

5. "Molecular decomposition of 2,2,3,3-tetramethylbutane".
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R. R. Baker, R. R. Baldwin, and R. W. Walker.
J. Chem. Soc., Faraday I, 1978, 74, 2229.

7. "Rate constants for hydrogen + oxygen system, and for H atoms OH radicals + alkanes".
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12. "Decomposition of 2,2,3-trimethylbutane in the presence of oxygen".
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13. "Rate constants for reactions of HO_2 radicals with alkanes, aldehydes, and related compounds".
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15. "The reactions of ethyl radicals with oxygen over the temperature range 400-540°C'.
R. R. Baldwin, I. A. Pickering, and R. W. Walker.
J. Chem. Soc., Faraday I, in the press.

16. "The addition of pentenes to slowly reacting mixtures of hydrogen and oxygen at 480°C".
R. R. Baldwin, Mrs. J. P. Bennett, and R. W. Walker.
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17. "The addition of 2,2,3-trimethylbutane to slowly reacting mixtures of hydrogen and oxygen at 480°C".
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J. Chem. Soc., Faraday I, submitted for publication.

Conferences attended and Lectures presented

Dr. Walker attended the "Fifth International Symposium on Gas Kinetics", held in Manchester in July 1977 and presented a paper entitled "The Decomposition of Tetramethylbutane in the Presence of Oxygen".

Professor Baldwin gave an invited lecture entitled "Problems and Progress in Hydrocarbon Oxidation", at the Autumn meeting of the Chemical Society, held at the University of Aberdeen in September 1977.

Professor Baldwin and Dr. Walker attended the Seventeenth (International) Combustion Symposium held at the University of Leeds in August 1978, and presented a paper entitled "Rate Constants for Reactions of HO_2 Radicals with Alkanes, Aldehydes, and Related Compounds".

Dr. Walker attended the U.S. Air Force Contractors' Meeting held at Dayton, Ohio, in October 1978, and presented a paper entitled "Rate Constants for H, OH, and HO_2 Radical Attack on Alkanes".

Professor Baldwin, Dr. Walker, and their research group attended a one-day research meeting on "Combustion" at the University of York in May 1979.

Professor Baldwin and Dr. Walker presented a paper entitled "Towards a Quantitative Interpretation of Gas-Phase Hydrocarbon Oxidation", at the meeting of the Gas Kinetics Discussion Group of the Chemical Society at Keele University in September 1979.

Professor Baldwin attended the U.S. Air Force Contractors' Meeting on "Air-Breathing Combustion Dynamics and Kinetics" held in Alexandria, Virginia, in January 1980, where he presented a paper entitled "Kinetics of Oxidation Reactions".

Dr. Walker attended the"Sixth International Symposium on Gas Kinetics" hald at Southampton in July 1980, and presented a paper entitled "Elementary Reactions in the Gas-Phase Oxidation of Alkenes".

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Personnel

Mrs. J. P. Bennett, who was financed under Grant AFOSR 73-2450, has successfully submitted for the Ph.D. degree.

Mr. R. W. Walker, financed by a Science Research Council Award, who joined the group in September 1975, has completed his period of study and has submitted his Ph.D. thesis. He has now taken up a position with Imperial Chemical Industries Ltd.

Mr. G. A. Evans, who joined the research group in 1975, and was financed under Grants AFOSR 73-2450 and AFOSR 77-3215, has completed his period of study and will shortly be submitting his Ph.D. thesis. He has now obtained a teaching post at Knaresborough Grammar School.

Mr. A. P. Keen (B.Sc., Hull 1977) joined the group in September 1977, financed by Grant AFOSR 77-3215.

Mr. I. A. Pickering (B.Sc., Hull 1978) who joined the research group as technician in July 1978, took up another appointment in January 1980.

Mr. D. G. Malcolm (B.Sc., Hull 1978) and Mr. M.W.M. Hisham (B.Sc., University of Sri Lanka) joined the research group in September 1978 and were financed by Grant AFOSR 77-3215. Mr. Malcolm has taken up the post of Research Assistant, financed by the Science Research Council, as from October 1979.

Miss A. Sutcliffe (B.Sc., Hull 1979) joined the research group in September 1979 and is financed under Grant AFOSR 77-3215.

Mr. P. H. Buck (B.Sc., University of Nottingham 1980) will join the group in August 1980 and will be financed under Grant AFOSR 77-3215.

Mr. G. R. Drewery (B.Sc., Hull 1980) will join the group in September 1980 and will be financed by a Science Research Council Award.

Mr. C. J. Cleugh, who was financed by the Science Research Council, has been awarded the degree of M.Sc.

The Science Research Council have made a grant of £33,050 to Professor Baldwin and Dr. Walker for the purchase of Perkin Elmer gas chromatographic equipment, and to provide for a Research Assistant.

Informal discussions have taken place with Professor Barnard of the University of Sheffield, Dr. Simmons of the University of Manchester Institute of Science and Technology, Professor Gray, Professor Williams, Personnel / continued

Professor Dixon-Lewis, Dr. Baulch, and Dr. Griffiths of Leeds University, Dr. Golden of the Stanford Research Institute, Professor Waddington of York University, Dr. Turner of Bradford University, Dr. D. Booth of Newcastle Polytechnic, Dr. Cohen of Drexel University, Professor Glassman and Dr. Dryer of Princeton University, and Dr. K. Booth of Imperial Chemical Industries Ltd.

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Appendix I

Rate Constants for the i-C_4H_9 Radical System at 480°C

Reaction		$k/dm^3,mol,s$	note
$CH_3CH(CH_3)CH_2$	$= C_3H_6 + CH_3$	8.8×10^4	
$CH_3CH(CH_3)CH_2 + O_2$	$= i\text{-}C_4H_8 + HO_2$	6.8×10^7	
$CH_3CH(CH_3)CH_2 + O_2$	$= CH_3CH(CH_3)CH_2O_2$	1.0×10^9	a
$CH_3CH(CH_3)CH_2O_2$	$= CH_3CH(CH_3)CH_2 + O_2$	2.6×10^6	b
$CH_3CH(CH_3)CH_2O_2$	$= CH_3CH(CH_2OOH)CH_2$	4.45×10^4	b
$CH_3CH(CH_2OOH)CH_2$	$= CH_3CH(CH_3)CH_2O_2$	1.35×10^6	b
$CH_3CH(CH_3)CH_2O_2$	$= CH_3C(CH_3)(CH_2OOH)$	1.83×10^5	b
$CH_3C(CH_3)(CH_2OOH)$	$= CH_3CH(CH_3)CH_2O_2$	8.3×10^5	b
$CH_3CH(CH_2OOH)CH_2$	= 3-methyloxetan + OH	$(1-2) \times 10^6$	c
$CH_3C(CH_3)(CH_2OOH)$	= isobutene oxide + OH	1.8×10^6	c
$CH_3CH(CH_2OOH)CH_2 + O_2$	$= CH_3CH(CH_2OOH)CH_2O_2$	1.0×10^9	a
$CH_3CH(CH_2OOH)CH_2O_2$	$= CH_3CH(CH_2OOH)CH_2 + O_2$	2.6×10^6	b
$CH_3C(CH_3)(CH_2OOH) + O_2$	$= CH_3C(CH_3)(CH_2OOH)O_2$	1.0×10^9	a
$CH_3C(CH_3)(CH_2OOH)O_2$	$= CH_3C(CH_3)(CH_2OOH) + O_2$	7.5×10^6	b
$CH_3CH(CH_2OOH)CH_2O_2$	$= CH_3CHO + 2HCHO + OH$	$(1-2) \times 10^6$	c
$CH_3C(CH_3)(CH_2OOH)O_2$	$= CH_3COCH_3 + HCHO + HO_2$	3.0×10^6	c
$CH_3C(CH_3)(CH_2OOH)$	$= CH_2{=}C(CH_3)CH_2OH + OH$	1.3×10^5	c
$CH_3C(CH_3)(CH_2OOH)$	$= CH_2{=}C(CH_3)CHO + OH + H_2$	1.3×10^5	c
$CH_3C(CH_3)(CH_2OOH)$	$= (CH_3)_2CHCHO + OH$	4.2×10^5	c

[a] Assumed value.

[b] The values are dependent on the calculated value of $K(R + O_2)$.

[c] The values are determined from maximum and minimum limits.

Appendix II

Rate Constants for the Oxidation of Pentane at 480°C

Reaction		k/s^{-1}	note
$CH_3CH_2CHCH_2CH_3$	$= CH_3CH_2CH{=}CH_2 + CH_3$	1.6×10^5	
$CH_3CHCH_2CH_2CH_3$	$= CH_3CH{=}CH_2 + C_2H_5$	2.3×10^5	
$CH_3CH(O_2)CH_2CH_2CH_3$	$= CH_3CH(OOH)CHCH_2CH_3$	4.7×10^4	
$CH_3CH(O_2)CH_2CH_2CH_3$	$= CH_3CH(OOH)CH_2CHCH_3$	3.0×10^5	
$CH_3CH(OOH)CH_2CHCH_3$	= 2,4-dimethyloxetan + OH	1.0×10^6	b
$CH_3CH(OOH)CH_2CH(O_2)CH_3$	$= 2CH_3CHO + HCHO + OH$	5×10^5	b
$CH_3CH_2CH_2CH_2CH_2 + O_2$	$= CH_3CH_2CH_2CH{=}CH_2 + HO_2$	2.9×10^8	a
$CH_3CH_2CH_2CH_2CH_2O_2$	$= CH_3CHCH_2CH_2CH_2OOH$	6.6×10^5	
$CH_3CH_2CH_2CH_2CH_2O_2$	$= CH_2CH_2CH_2CH_2CH_2OOH$	9.3×10^4	
$CH_3CH_2CHCH_2CH_2OOH$	= 2-ethyloxetan + OH	1.0×10^6	b
$CH_3CH_2CH(O_2)CH_2CH_2OOH$	$= C_2H_5CHO + 2HCHO + OH$	8×10^5	b

[a] Units, $dm^3\ mol^{-1}\ s^{-1}$.

[b] Values determined from maximum and minimum limits.