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BY RR BALDWIN & RW WALKER

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

1) There has been a continuing refinement in the interpretation of the second limit (using mixtures with very low concentrations of O_2) and slow reaction (making allowance for self-heating) of $H_2 + O_2$ mixtures at 500°C. Studies of $CO + H_2 + O_2$ mixtures have given rate constants for reactions of CO with radicals. 2) Studies of the addition of alkanes and related compounds to slowly reacting mixtures of $H_2 + O_2$ have continued. The mechanism for the formation of conjugate alkene has been elucidated, and the rate constants of a large number of elementary reactions have been determined. 3) Studies have been made of the oxidation of

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HCHO, CH_3CHO, C_2H_5CHO, n- and i-C_3H_7CHO, and the rate constants evaluated for a number of the elementary steps involved. 4) The homogeneous decomposition of hexamethylethane has been studied over the temperature range 440-540°C as a potential source both of t-butyl radicals and of HO_2 radicals. 5) A detailed study and interpretation has been made of the reaction between H_2 and N_2O at temperatures of 500°C and 600°C. Rate constants for some of the elementary steps have been obtained.

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FINAL SCIENTIFIC REPORT

Kinetics of Hydrogen-Oxygen and Hydrocarbon-Oxygen Reactions

1st October 1972 - 31st March 1977

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

Chemistry Department,
The University,
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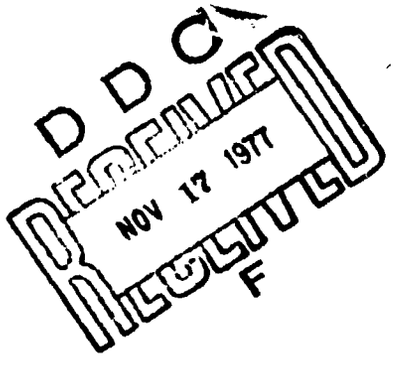

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I N D E X

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Final Report under Grant No. AFOSR-73-2450

October 1972 - March 1977

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

SUMMARY

During the four year period of the present grant, quantitative information has been obtained on a wide range of reactions involved in combustion processes. Work has concentrated into five main areas of investigation.

(1) There has been a continuing refinement in the interpretation of the second limit and slow reaction of $H_2 + O_2$ mixtures at temperatures around 500°C, and increased precision in the establishment of rate constants at this temperature. This has been achieved by an examination of the second limit at very low concentrations of O_2 (section 1a) and allowance for the occurrence of self-heating in the slow reaction (section 1b). Study of the second limit (section 1c) and slow reaction (section 1d) of $CO + H_2 + O_2$ mixtures has given information on the rate constants for reactions of CO with radicals that play a part in carbon monoxide oxidation.

(2) Studies of the addition of alkanes and related compounds to slowly reacting mixtures of $H_2 + O_2$ have continued. In isolating more accurate rate constants for the H and OH radical reactions with the alkanes, allowance has been made for self-heating and attack by O atoms and HO_2 radicals. The mechanism for the formation of conjugate alkene has been elucidated, and the rate constants of a large number of elementary reactions have been determined.

(3) Studies have been made of the oxidation of HCHO, CH_3CHO, C_2H_5CHO, n- and i-C_3H_7CHO. The results have been interpreted in varying degrees of detail, and rate constants evaluated for a number of the elementary steps involved.

(4) The homogeneous decomposition of hexamethylethane has been studied over the temperature range 440 - 540°C as a potential source both of t-butyl radicals and of HO_2 radicals. The Arrhenius parameters for the decomposition have been used to obtain values for the standard entropy and enthalpy of formation of these radicals. Rate constants for the reactions of these radicals have been evaluated.

(5) A detailed study and interpretation has been made of the reaction between H_2 and N_2O at temperatures of 500°C and 600°C. A separate evaluation of the rate constant for the important elementary step $H + N_2O = N_2 + OH$ has been made by measurement of N_2 formation when N_2O is added to slowly reacting mixtures of $H_2 + O_2$.

--ooOoo--

1. The hydrogen + oxygen reaction

During the present grant period, studies of the $H_2 + O_2$ reaction have continued, either to refine values of the rate constants at temperatures around 500°C for the elementary steps, or to use the reaction to study reactions of radicals with CO. The use of the $H_2 + O_2$ reaction to study the elementary steps in hydrocarbon oxidation is described in section 2.

(a) Second limit of $H_2 + O_2$ mixtures

Previous studies[1,2] have shown that the second limit, and the induction period and maximum rate of $H_2 + O_2 + N_2$ mixtures at 500°C can be interpreted with considerable precision by the mechanism given below. Computer programmes have been used to obtain values of the rate constants or rate constant ratios which give the best agreement between the observed measurements and the calculated values.

OH	+	H_2	=	H_2O	+	H	(1)
H	+	O_2	=	OH	+	O	(2)
O	+	H_2	=	OH	+	H	(3)
H +	O_2 +	M	=	HO_2	+	M	(4)
H_2O_2	+	M'	=	2OH	+	M'	(7)
H	+	HO_2	=		2OH		(8)
	$2HO_2$		=	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)

However, careful examination shows that the observed second limits at very low concentrations of O_2 (<0.02 mole fraction) are consistently below the calculated limit, the discrepancy increasing

as the O_2 mole fraction is reduced. Use of the computer programme for calculation of the second limit, with additional reactions included, shows that this discrepancy can be removed by including a contribution either from reaction (8a), or from surface destruction of H atoms.

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

$$H \xrightarrow{\text{surface}} \tfrac{1}{2}H_2 \qquad (H)$$

The effect of reaction (8a) is shown in Table 1, which gives, for a range of values of $k_{8a}/k_2k_{10}^{\frac{1}{2}}$, the optimum value of $k_8/k_2k_{10}^{\frac{1}{2}}$ required to give minimum r.m.s. deviation between observed and calculated values of the second limit for 13 mixtures covering the range 0.0044 - 0.72 mole fraction O_2.

Table 1

Effect of Reaction (8a) on the Second Limit

$(k_{8a}/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	0	1	2	3	4	5
Optimum value of $(k_8/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	9.22	11.65	14.15	16.65	19.20	22.8
% r.m.s. deviation	4.00	2.05	0.84	2.01	3.59	5.7

Table 2 shows the effect of introducing surface destruction of H atoms, with a range of values of k_H/k_2.

Table 2

Effect of Surface Destruction of H Atoms

$(k_H/k_2)/\text{Torr}$	0	0.1	0.2	0.3	0.4	0.5
Optimum value of $(k_8/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	9.22	9.71	10.24	10.82	11.47	12.21
% r.m.s. deviation	4.00	3.17	2.26	1.28	0.73	1.82

The low r.m.s. deviations do not permit distinction between the alternatives $k_H/k_2 = 0$, $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 2.0$ (Torr min)$^{\frac{1}{2}}$, and $k_H/k_2 = 0.4$ Torr, $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 0$, or any intermediate combinations. However, the value of $k_H/k_2 = 0.4$ implies a partial pressure of 0.2 Torr of O_2 at the first limit, equivalent to 1.5 Torr for the standard mixture (0.28, 0.14, 0.58 mole fractions of H_2, O_2, N_2, respectively). However, careful study of the first limit[3] showed that visible emission could be detected down to 0.4 Torr, and that pressure kicks could be detected on a sensitive transducer down to pressures of about 0.1 Torr. It can thus be concluded that the contribution from surface destruction can be neglected at the second limit.

$$H + HO_2 = H_2O + O \qquad (8b)$$

The computer programme was also used to examine the effect of reaction (8b), and it was found that this reaction is extremely similar kinetically to reaction (8).

The effect of introducing the reaction $O + H_2O_2$ was also examined.

$$O + H_2O_2 = H_2O + O_2 \qquad (13)$$

$$O + H_2O_2 = OH + HO_2 \qquad (13a)$$

Albers et al.[4] give $(k_{13} + k_{13a}) = 2.8 \times 10^{10} \exp(-3220/T)$, which combined with $k_3 = 1.8 \times 10^7 T \exp(-4480/T)$[5] gives $(k_{13} + k_{13a})/k_3 = 10.4$ at 500°C. The maximum effect of $O + H_2O_2$ occurs if $k_{13a} = 0$, when the optimum value of $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ is 2.7 (Torr min)$^{\frac{1}{2}}$, with $k_8/k_2k_{10}^{\frac{1}{2}} = 16.2$ (Torr min)$^{\frac{1}{2}}$ and a r.m.s. deviation of 1.65%. If $k_{13} = 0$, and $k_{13a}/k_3 = 10.4$, the values are midway between those with $(k_{13} + k_{13a})/k_3 = 0$, and with $k_{13}/k_3 = 10.4$, $k_{13a}/k_3 = 0$. By combining the values of k_{8a}/k_8 and k_{8b}/k_8 obtained by other workers, the recommended Arrhenius parameters[3] are $A_8 = 2.8 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, $E_8 = 1.7$ kcal mol^{-1}, $A_{8a} = 1.7 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $E_{8a} = 0$, $A_{8b} = 2.8 \times 10^{10}$, $E_{8b} = 1.7$ kcal mol^{-1}. It is interesting that the O-O fission reaction both for $H + HO_2$ and for $H + H_2O_2$ has the higher activation, since $E_{14} - E_{14a} \approx 4$ kcal mol^{-1}. This work has been published[3].

(b) Rate constants of the $H_2 + O_2$ reaction

Continuing intermittent attempts have been made to measure

experimentally the small temperature rise (1-2°C) occurring in slowly reacting $H_2 + O_2 + N_2$ mixtures at 500°C, but confidence in the results is not sufficient to justify publication at the present. A computer programme which allows for this self-heating is being used to examine the effect of the self-heating on the parameters $k_{11}/k_{10}^{\frac{1}{2}}$, k_{14}/k_2 and k_{15}/k_1, that are obtained from studies of the induction period and maximum rate of the slow reaction. The effect of the reactions (8a), (13) and (13a), introduced in section (1a), is also being examined. The calculations suggest that the finally recommended values of these parameters will be within 10% of those recommended in earlier papers[1,2].

(c) The effect of CO on the second limit of $H_2 + O_2 + N_2$ mixtures

The second limit of $H_2 + O_2 + N_2$ mixtures, in which CO has been interchanged with N_2, has been studied over a wide concentration range. Difficulties have been found in the use of KCl-coated and CsCl-coated vessels, and aged boric-acid-coated vessels were eventually used. To interpret the results using a computer, four reactions need to be added to the mechanism for the second limit used in section (1a).

CH	+	CO	=	CO_2	+	H			(21)
H	+	CO	+ M"	=	HCO	+	M"		(22)
(HCO	+	O_2	=	HO_2	+	CO)			
O	+	CO	+ M"'	=	CO_2	+	M"'		(23)
HO_2	+	CO	=	CO_2	+	OH			(24)

In addition to the four parameters k_{21}/k_1, k_{22}/k_4, k_{23}/k_3 and $k_{24}/k_{10}^{\frac{1}{2}}$, the efficiency of CO relative to H_2 in reaction (4), $m_{4(CO)}$, is also required to operate the computer programme. Only two of these parameters, k_{22}/k_4 and $m_{4(CO)}$ have any significant effect on the limit, and it is not feasible to evaluate the others from the present studies.

A value of $k_{23}/k_3 = 8.5$ litre mol^{-1} at 500°C has been obtained[6] by interpreting measurements made by Buckler and Norrish of the second limit of $2CO + O_2$ mixtures in the presence of small amounts (up to 10%) of H_2; in interpreting the results, it has been assumed that CO and O_2 have the same efficiency relative to H_2 in reactions (4) and (23), and

the value quoted for k_{23}/k_3 refers to M = H_2. From the recommended values[7] of k_3, k_{23} = 3.1 x 10^8 dm^6 mol^{-2} s^{-1} at 500°C. Use of the more recent recommendation[5] for k_3 gives k_{23} = 3.6 x 10^8 dm^6 mol^{-2} s^{-1}. The relationship of this value to other evaluations is discussed in the published paper[6]. Slight changes in these values, dependent on the value assumed for $m_{23(CO)}$, and on the possible pressure dependence of k_{23}, are discussed in a later paper[8].

Computer treatment also shows that the limit is relatively insensitive to the values used for k_{21}/k_1 and $k_{24}/k_{10}^{\frac{1}{2}}$, and that these can be obtained with ample accuracy from the work described in section (1d). The variation of limit can thus be used to evaluate k_{22}/k_4 and $m_{4(CO)}$. The former parameter is most important at low O_2 concentrations, so that studies in the range $[O_2]$ = 0.0088 - 0.14 were made. An optimisation procedure was incorporated in the computer programme to adjust the values of k_{22}/k_4 and $m_{4(CO)}$ to give minimum r.m.s. deviation between observed and calculated limits. The optimum values of k_{22}/k_4 = 0.0225, $m_{4(CO)}$ = 0.74 gave a r.m.s. deviation of 1.1%. The value of k_{22} refers to M" = H_2 and in calculations it has been assumed that the coefficients of N_2 and O_2 relative to H_2 are the same in reactions (4) and (22), and that the coefficient for CO is the same as for N_2. From the known value of k_4, k_{22} = 2.3 x 10^8 dm^6 mol^{-2} s^{-1} at 500°C. The determination of $m_{4(CO)}$ is valuable both for the work described in section (1d), and in interpreting results obtained on the H_2O-sensitised reaction of CO + O_2 mixtures.

(d) Slow reaction of CO + H_2 + O_2 mixtures

By interchanging CO with N_2, the effect of a wide range of carbon monoxide concentrations on the induction period and on the rate of the slow reaction of H_2 + O_2 + N_2 mixtures has been examined over a wide range of concentrations of H_2 and O_2 at 500°C and a total pressure of 500 Torr. The maximum rate of the slow reaction is increased by factors of up to 5, and the induction periods are decreased by similar factors. The results have been interpreted by the use of a computer programme applied to a mechanism in which reactions (21) - (24) have been added to the basic mechanism of the H_2 + O_2 reaction at 500°C given in section (1a). Use of the computer programme shows that the

maximum rate is insensitive to k_{21}/k_1 and k_{22}/k_4, and is only slightly sensitive to k_{23}/k_3 and to $m_{4(CO)}$ for mixtures of low H_2 content and high CO content. For all mixtures, the change in rate on addition of CO is almost entirely determined by the parameter $k_{24}/k_{10}^{\frac{1}{2}}$, so that its accurate evaluation is not critically dependent on the values taken for the other parameters involving CO. Evaluation of these parameters has been discussed in section (1c). The change in induction period is also predominantly determined by the parameter $k_{24}/k_{10}^{\frac{1}{2}}$, although $m_{4(CO)}$ has a more marked effect than on the rate, and reaction (23) has a small effect at high $[CO]/[N_2]$ ratios.

Use of the computer programme to compare observed and calculated values of the maximum rate for 29 mixtures with H_2 content of 140 Torr or greater gave the optimum value of $k_{24}/k_{10}^{\frac{1}{2}} = 0.411$ $(dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$ at 500°C, with an r.m.s. deviation of 1.5% between observed and calculated rates. The corresponding value for 33 mixtures of lower H_2 content (70 Torr or less) was 0.488 with an r.m.s. deviation of 4.6%. A value of $k_{24}/k_{10}^{\frac{1}{2}} = 0.48$ is required to give the best interpretation of the induction period for both sets of mixtures; however, this value is considered less reliable, as increasing CO has less effect on the induction periods and the calculated induction periods also become less sensitive, under these conditions, to the value of $k_{24}/k_{10}^{\frac{1}{2}}$. The best value of $k_{24}/k_{10}^{\frac{1}{2}}$ is considered to be 0.425 ± 0.03 $(dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$. This value is obtained by using the value of $k_{23}/k_3 = 1.8\ dm^3\ mol^{-1}$ $[M = N_2]$, obtained from the experimental results discussed in section (1c) but modified as discussed in reference 8. Use of the lower value of 0.9, obtained from independent estimates of k_{23} and k_3, and which is considered less reliable, only decreases $k_{24}/k_{10}^{\frac{1}{2}}$ by about 3%. From the known value of $k_{10} = 2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, $k_{24} = 1.9 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$. Combination with a value of $k_{24} = 5.45 \times 10^3$, obtained at 440°C from a study[9] of the CO-sensitised decomposition of H_2O_2, suggests that $E_{24} = 23$ kcal mol^{-1}, consistent with a value suggested by Vardanyan, Sachyan and Nalbandyan[10]. With this value of E_{24}, the present value of k_{24} gives $A_{24} = 6.0 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$. This work has been accepted for publication[8].

(e) CO_2 yields in slowly reacting $CO + H_2 + O_2$ mixtures

Opportunity has also been taken to use the computer programme to

re-interpret some earlier results on the relative yields of CO_2 and H_2O when small quantities of CO are added to slowly reacting mixtures at 500°C. The original data were obtained using 1% of CO, and the CO_2 analysis was made using a vacuum analysis method. New data have been obtained with 0.5% CO, and CO_2 formation was determined gas chromatographically. The relative yields of CO_2 and H_2O (calculated from the pressure change) are determined by the parameters k_{21}/k_1 and $k_{24}/k_{10}^{\frac{1}{2}}$, and both parameters can be evaluated if a range of $[H_2]/[O_2]$ ratios is used. Use of the computer treatment to obtain minimum r.m.s. deviations between observed and calculated $[CO_2]/[H_2O]$ ratios gives $k_{24}/k_{10}^{\frac{1}{2}} = 0.42 \pm 0.03$ $(dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$, $k_{21}/k_1 = 0.233 \pm 0.02$ for the original observations, and $k_{24}/k_{10}^{\frac{1}{2}} = 0.41 \pm 0.03$, $k_{21}/k_1 = 0.230 \pm 0.02$ for the new set, with minimum r.m.s. deviations of 3.6 and 3.4%, respectively. However, when both parameters are optimised, a rather flat minimum in the r.m.s. deviation is obtained, and it has been considered more accurate to accept the value of $k_{24}/k_{10}^{\frac{1}{2}}$ obtained in section (1d), and to optimise with respect to k_{21}/k_1, when an optimum value of $k_{21}/k_1 = 0.23 \pm 0.02$ is obtained.

Using published data over the range 300 - 900 K, the log k_1, 1/T plot is slightly curved, but a well defined value of $k_1 = (4.1 \pm 0.4) \times 10^8$ at 500°C can be obtained, giving $k_{21} = (0.96 \pm 0.2) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$ at 500°C. This work has been accepted for publication[8].

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

(a) Rate constants for attack by H and OH radicals on alkanes

The previous Final Report[14] listed values of rate constants for the reactions of H and OH radicals with C_2 - C_4 alkanes obtained from studies of the relative rate of loss of alkane and H_2 when traces (<0.1%) of the alkane are added to slowly reacting mixtures of $H_2 + O_2$ in aged boric-acid-coated vessels at 480°C. However, as indicated previously[14], the values require correction for self-heating (1 - 2°C)[15] because of its effect on the values of the observed pressure change, used to determine the loss of H_2. Allowance for self-heating has now been made[16] by a computer interpretation, which also incorporates the full mechanism for the $H_2 + O_2$ reaction and attack by O atoms and HO_2 radicals, as well as H and OH, on the alkane. The corrected values at 480°C are given in Table 3.

Table 3

alkane	k_{21}/k_1	k_{21} / $dm^3\ mol^{-1}\ s^{-1}$	k_{22}/k_2	k_{22} / $dm^3\ mol^{-1}\ s^{-1}$
C_2H_6	5.8	3.2×10^{10}	43.5	2.5×10^{8}
C_3H_8	9.6	5.3×10^{10}	125	7.2×10^{8}
$n\text{-}C_4H_{10}$	12.8	7.0×10^{10}	217	12.6×10^{8}
$i\text{-}C_4H_{10}$	12.3	6.8×10^{10}	223	12.9×10^{8}

Use of the most recent[11-13] values for k_1 gives $k_1 = (5.5 \pm 0.5) \times 10^9$ at 480°C and the absolute values of k_{22} are based on k_{22}/k_2 and Camilleri, Marshall, and Purnell's[17] expression for $k(H + C_2H_6)$. Combination with independent estimates gives Arrhenius parameters for overall attack.

OH	+	H_2	=	H_2O	+	H (1)
H	+	O_2	=	OH	+	O (2)
OH	+	RH	=	R	+	H_2O (21)
H	+	RH	=	R	+	H_2 (22)

For a quantitative interpretation of the products from hydrocarbon oxidation, it is necessary to calculate the proportion of each species of alkyl radical formed from the radical attack on the alkane. Use is made of the additivity rule, which assumes that all primary C - H bonds, all secondary C - H bonds and all tertiary C - H bonds in alkanes are equivalent, and which leads to the following expression for the overall rate constant.

$$k = n_p A_p \exp(-E_p/RT) + n_s A_s \exp(-E_s/RT) + n_t A_t \exp(-E_t/RT)$$

The subscripts p, s, t, refer to attack at primary, secondary, and tertiary C - H bonds, and n is the number of C - H bonds. Preliminary values of A(per C - H bond) and E have been determined[14,18,19] for H, OH, and HO_2 attack on alkanes, and final values are currently being computed[16]. At 480°C, use of the parameters in Table 3 allows a precise calculation of the relative proportions of each species of alkyl radical formed in H and OH attack. For the temperature range 300 - 650°C, the calculated proportions will be quite accurate if Table 3 is used in conjunction with activation energies given earlier[18,19] for H and OH attack.

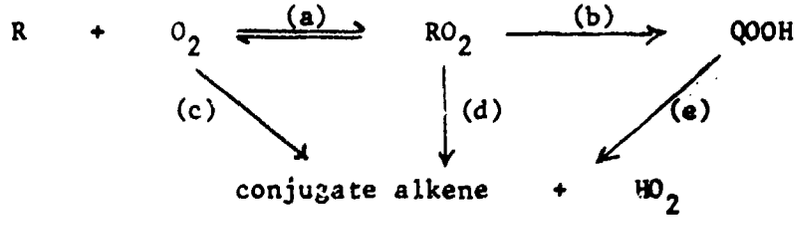
(b) Addition of propane, butane, and neopentane

Details of the products formed when traces of propane, butane, and neopentane are added to slowly reacting mixtures of $H_2 + O_2$ have been given in previous reports[14]. Elucidation of the mechanism of hydrocarbon oxidation continues, and considerable progress has been made, often with the aid of more recent and independent work. Advances have also been made particularly in the chemistry of the formation of conjugate alkene and O-heterocyclic compounds, which often account for over 90% of the alkane consumed in the initial stages.

Recent studies[20] with n-butane as additive using fresh and aged boric-acid-coated and 'clean' Pyrex vessels with diameters varying between 20 and 52 mm i.d., have shown that the product ratios [conjugate alkene]/[lower alkene] and [conjugate alkene]/[O-heterocyclic compounds] are independent of vessel diameter and surface. It is concluded that surface processes are not involved at normal pressures in product formation at 480°C, and this conclusion almost certainly holds at higher temperatures. At lower temperatures, about 250 - 300°C,

surface reactions of RO_2, and particularly ROOH, may well be important in the formation of oxygenated products with a lower carbon number than the parent alkane.

Although, despite suggestions to the contrary[21,22], it is now established that conjugate alkene is formed in the gas phase, the mechanism is not unambiguously established and three routes are possible as shown in the following scheme.



Studies[23] of the separate addition of n-butane and cis-but-2-ene have established that the conjugate alkene is formed either in the direct bimolecular reaction (c), or via RO_2, but not from the decomposition of QOOH radicals, formed from RO_2 radicals by H atom transfer (see later). As R and RO_2 are effectively equilibrated under nearly all conditions at about 500°C, the two routes for formation are kinetically equivalent. The balance of evidence[24] supports the direct bimolecular reaction, and on this basis, rate constants for the formation of conjugate alkenes from a number of alkyl radicals are given in Table 4.

Table 4

Rate constants for the formation of conjugate alkene

Reaction	Product	T/°C	k/dm^3 mol^{-1} s^{-1}
$C_2H_5 + O_2$	C_2H_4	440	5.5×10^7
		623	1.0×10^8 *
$n\text{-}C_3H_7 + O_2$	C_3H_6	450	1.8×10^7
		480	2.2×10^7
$i\text{-}C_3H_7 + O_2$	C_3H_6	440	1.3×10^8
$n\text{-}C_4H_9 + O_2$	C_4H_8-1	480	1.6×10^8
$s\text{-}C_4H_9 + O_2$	trans-C_4H_8-2	480	7.8×10^7
	cis-C_4H_8-2	480	4.3×10^7
	C_4H_8-1	480	5.1×10^7
$i\text{-}C_4H_9 + O_2$	$i\text{-}C_4H_8$	480	5.8×10^7 **
		40	9.9×10^4 +

* R. J. Sampson, J. Chem. Soc., 1963, 5095

** Preliminary value

\+

Combination of the two values for i-butyl + O_2 gives A = 7.2×10^9 $dm^3\ mol^{-1}\ s^{-1}$ and E = 6.8 kcal mol^{-1}. Virtually no independent data are available for reaction (c). As the value of E_c is small, and unlikely to vary significantly for the different alkyl radicals, relatively reliable values of k_c over the temperature range 300 - 650°C can be obtained by combining the values of k_c at 480°C in Table 4 with the activation energy for i-butyl + O_2. It should, however, be realised that the values of k_c are ultimately dependent on the values used[18] for radical-radical recombination; the presently recommended values[18] are $10^{10.0}$, $10^{9.5}$, and $10^{9.0}$ for primary, secondary, tertiary alkyl radicals, respectively.

O-heterocyclic compounds are frequently formed in high yield, particularly at temperatures near 300°C and with alkanes containing a carbon number in excess of 4. Studies with neopentane[25], n-butane, and cis- and trans-but-2-ene[23] have established the peroxy radical isomerisation and decomposition (PRID) sequence of reactions as the mechanism of formation.

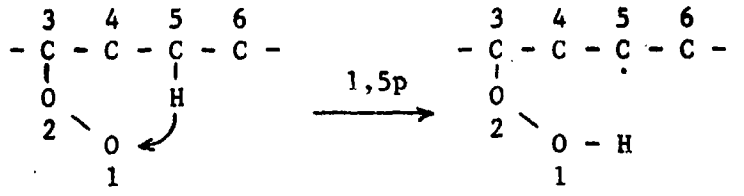
$$R + O_2 \underset{}{\overset{(a)}{\rightleftharpoons}} RO_2 \xrightarrow{(b)} QOOH \xrightarrow{(f)} \text{O-heterocycle} + OH$$

$$RO_2 \xrightarrow{(g)} \text{decomposition products}$$

From measurements of the variation of the relative yields of cracking products and O-heterocyclic compounds with mixture composition, rate constants for the elementary steps involved have been obtained from the following general equation.

$$\frac{d[\text{O-heterocycle}]}{d[\text{cracking product}]} = \frac{K_b k_f [O_2]}{k_g}$$

By the use of Benson's[26] additivity rules to calculate K_a and literature values for k_g[18], modified to account for recent determinations of radical-radical rate constants[18], values of k_f have been obtained for a number of different H atom transfers in RO_2 radicals. The recommended values are shown in Table 5; no other experimental values are available. In Table 5, a 1,5p transfer would refer to a transition involving a primary C - H bond in the following way:



In general, the values of k_b at 480°C differ by two orders of magnitude from those estimated theoretically by Fish[27], and are consistent with the yields of O-heterocyclic compounds in the oxidation of a large number of alkanes over the temperature range 250 - 550°C. The activation energies given in column A are based on an A factor of $10^{12.1}$ s^{-1} for all H atom transfers. Recently, it has been suggested[28] that the A factor should decrease with increase in the ring size in the transition state, and column B gives activation energies for A(1,4) = $10^{13.1}$, A(1,5) = $10^{12.1}$, and A(1,6) = $10^{11.1}$ s^{-1}.

Table 5

Rate constants for the formation of QOOH radicals at 480°C

Transfer	k_b/s^{-1}	E_b/kcal mol^{-1}	
		A	B
1,4p	2.2×10^3	30	33.5
1,4s	2.4×10^4	26.5	30
1.4t	2.6×10^5	23	26.5
1,5p	1.8×10^4	27	27
1,5s	2.0×10^5	23.5	23.5
1,5t	2.2×10^6	20	20
1,6p	6.0×10^4	25	21.5
1,6s	6.5×10^5	21.5	18
1,6t	7.1×10^6	18	14.5

A reinterpretation[29] of results obtained by Eucker and Leinroth[30] from the oxidation of n-butane at 325°C gives a value for k(1,4s) = 53 s^{-1}. Combination with the value at 480°C gives A(1,4s) = 5×10^{12} s^{-1} and E(1,4s) = 30 kcal mol^{-1}, in excellent agreement with the parameters given in Table 5. The reinterpretation also confirms the importance

of radical-radical reactions as major propagation processes at high reaction rates, such as those observed during the passage of cool flames.

Due to their relatively high concentration, RO_2 radicals are prominent in radical-radical processes, and alkoxy radicals are formed in reactions such as

$$R' + RO_2 = 2RO$$
$$RO_2 + R'O_2 = RO + R'O + O_2$$

Although reactions of alkoxy radicals must, therefore, play a key part in the product distribution, relatively little kinetic information is available for these radicals; further studies in this area are planned.

Considerable evidence[23,25] has also been obtained to show that QOOH radicals are sufficiently stable at 480°C to add a further molecule of O_2, and rate constants have been determined for a number of elementary reactions involving the $(CH_3)_2C(CH_2OOH)CH_2$ radical[25]. The oxidative chemistry of acetone, 3,3-dimethyloxetan, isobutene, isobutyraldehyde and other products from neopentane has been studied[31] by the use of these compounds as additives. Rate constants for a number of the elementary reactions involved have been determined.

(c) Addition of n-pentane and hexamethylethane

A detailed experimental study of the addition of n-pentane to slowly reacting mixtures of $H_2 + O_2$ at 480°C has been completed. For a mixture containing 5, 70, 140 and 285 Torr of pentane, O_2, H_2, and N_2, respectively, the major hydrocarbon products are trans pentene-2 (20% mole/mole pentane consumed), cis pentene-2 (6%), pentene-1 (17%), butene-1 (6%), C_3H_6 (20%), C_2H_4 (16%) and CH_4 (12%). The hydrocarbons thus account for about 80% of the pentane removed in the early stages of reaction, the remainder being largely converted into O-heterocyclic compounds, tetrahydropyran (1.5%), 2-methyltetrahydrofuran (10%), 2,4-dimethyloxetan (7%), 3-ethyloxetan (2%), 1,2-epoxybutane (0.5%), 2,3-epoxybutane (3%). The yields of products are not particularly sensitive to mixture composition, although that of CH_3CHO increases significantly at high O_2, and the kinetics suggest that it is formed in direct competition with 2,4-dimethyloxetan. The very high yields of

acetone observed at 300°C are not found at 480°C.

A complementary study has also been made of the products formed when pentene-1 and pentene-2 are used separately as additives. The yield of cracking products from the pentenes is considerably higher than from n-pentane due to the rapid decomposition of vibrationally-excited pentyl radicals formed by H-atom addition to the pentenes.

$$H + CH_2{=}CHCH_2CH_2CH_3 \rightarrow \begin{cases} CH_3CHCH_2CH_2CH_3^* \rightarrow CH_3CH{=}CH_2 + C_2H_5 \\ CH_2CH_2CH_2CH_2CH_3^* \rightarrow C_2H_4 + CH_2CH_2CH_3 \end{cases}$$

The product distribution, determined under virtually identical radical conditions to those for the n-pentane studies, is of great importance in the establishment of the oxidative mechanisms of the pentyl radicals formed from n-pentane.

A computer programme has been written to interpret the observed distribution of the 27 products from n-pentane. No rate constants are available in the literature for any reaction of pentyl radicals of importance in this system. It was, therefore, decided to investigate how closely the rate constant data obtained from studies of the addition of C_2 - C_4 alkanes and neopentane could predict the yields of the products when n-pentane is the additive. For this preliminary analysis only the yields at 10% loss of pentane were considered. Use of the specific parameters for H, OH, O, and HO_2 attack on alkanes (section 2a) permits calculation of the proportions of 1-pentyl, 2-pentyl, and 3-pentyl formed, and hence of the proportions of the products fromeach species of pentyl radical. The calculated percentage yields are shown in Table 6, together with the experimental yields at 10% loss of n-pentane. The agreement is within a factor of about 2 for all products, which collectively account for over 90% of the pentane consumed. Clearly, by minor adjustments of rate constants, the agreement could be improved considerably, particularly in the relative yields of the pentenes and in the total yield of the cracking products, which is slightly too high. The predicted yields of the oxetans can be improved considerably if allowance is made for the formation of CH_3CHO and C_2H_5CHO by alternative reactions of QOOH radicals with O_2.

The role of alkyl radical isomerisation in the pentane system has also been considered. The only important isomerisation will be

$$\text{1-pentyl} \longrightarrow \text{2-pentyl}$$

for which Arrhenius parameters of A = 1.0×10^{11} s^{-1} and E = 20.3 kcal mol^{-1} have been reported[32]. The modified yields of products are shown in the final column in Table 6, and it is clear that isomerisation reactions are unimportant in pentane oxidation under normal conditions unless the rate constants for these processes are considerably higher than given above. Aspects of this work were presented at the Sixteenth International Symposium on Combustion held at Boston in August 1976[19].

Work is in progress with hexamethylethane as additive. Kinetic studies using 0.025% of the alkane have been completed, and the results are being processed by the use of a computer treatment to obtain the best values for the rate constants for H and OH attack on hexamethylethane. The values, compared to those for C_2H_6 and neopentane, are of considerable interest in relation to the additivity rule discussed in section (1a). Analytical studies with 1% of alkane show that the hexamethylethyl radical, formed in the primary attack, decomposes almost uniquely to give isobutene and the t-butyl radical, even in the presence of almost an atmosphere of O_2 at 480°C. As discussed in section (5), about 99% of the t-butyl radicals react with O_2 to form isobutene, which is therefore the only major initial product. Small amounts (ca. 1%) of 2,3,3-trimethylbutene-1 are also formed, the yield relative to that of isobutene increasing almost directly with the pressure of O_2. Preliminary analysis of the results suggests that it should be possible to isolate the elementary steps involved and so determine rate constants. Information obtained from this system is of importance to the interpretation of the results from the study of the decomposition of hexamethylethane in KCl-coated vessels discussed in section (5).

Table 6

Predicted and experimental yields of products from pentane

O_2 = 70, H_2 = 140, n-pentane = 5, N_2 = 285 Torr; T = 753 K

	Predicted yields				Exptl. yield at 10% loss	Predicted yield with isomerisation
	1-pentyl (22%)[a]	2-pentyl (52%)[a]	3-pentyl (26%)[a]	Total yield		
pentene-1	5.15	6.1	-	11.25	17.3	11.0
pentene-2	-	14.5	17.4	31.9	25.7	32.4
butene-1	-	-	7.3	7.3	5.8	7.3
propene	1.7	9.6	-	11.3	19.2	11.5
ethylene	3.5	9.6	-	13.1	15.8	13.2
methane	0.7	-	5.5	6.2	11.5	6.1
1,2-epoxybutane	0.35	0.17	-	0.52	0.41	0.50
2,3-epoxybutane	-	1.85	0.73	2.58	2.98	2.64
3-ethyloxetan	2.97	-	0.54	3.51	1.88	3.27
2,4-dimethyloxetan	-	15.2	-	15.2	7.3	15.8
2-methylTHF	9.61	4.6	-	14.2	10.4	13.6
THP	1.35	-	-	1.35	1.35	1.25

[a] percentage of pentyl radical formed from n-pentane

3. The High Temperature Oxidation of Aldehydes

(a) The oxidation of formaldehyde in KCl-coated vessels

Previous studies of the oxidation of HCHO in aged boric-acid-coated vessels have been described in an earlier report[14]. The reaction is significantly autocatalytic because of the dissociation of the product H_2O_2, so that the system is not a particularly convenient source of HO_2 radicals because of the presence of OH radicals also. H_2O_2 is destroyed fairly effectively in KCl-coated vessels, so that a simpler mechanism involving reactions (1) - (5) should operate.[33,34]

$HCHO$	+	O_2	=	HO_2	+	HCO	(1)
HCO	+	O_2	=	HO_2	+	CO	(2)
HO_2	+	$HCHO$	=	H_2O_2	+	HCO	(3)
	HO_2		surface =	$\frac{1}{2}H_2O$	+	$\frac{3}{4}O_2$	(4)
HO_2	+	HO_2	=	H_2O_2	+	O_2	(5)
	H_2O_2		surface =	H_2O	+	$\frac{1}{2}O_2$	(6)
H_2O_2	+	M	=	$2OH$	+	M	(7)
OH	+	$HCHO$	=	H_2O	+	HCO	(8)

If reactions (6) - (8) are neglected, there are three extreme possibilities.

(a) If the chain length is zero, the rate is given by expression (i).

$$d[CO]/dt = k_1[HCHO][O_2] \qquad \text{(i)}$$

(b) If reaction (5) is the sole termination process, the rate is given by expression (ii).

$$d[CO]/dt = k_1[HCHO][O_2] + k_2(k_1/k_5)^{\frac{1}{2}}[HCHO]^{3/2}[O_2]^{\frac{1}{2}} \qquad \text{(ii)}$$

(c) If reaction (4) is the sole termination process, the rate is given by expression (iii).

$$d[CO]/dt = k_1[HCHO][O_2] + (2k_1k_2/k_4)[HCHO]^2[O_2] \qquad \text{(iii)}$$

For HCHO concentrations in the range 1-4 Torr, 30 Torr of O_2, and a total pressure of 60 Torr with N_2, the order in HCHO is 1.8, which is

significantly above the order of 1.5 given by equation (ii), so that surface termination must also be important. However, calculations show that with 2 Torr of HCHO, the chain length is only about 2 - 3. Consequently, at sufficiently low concentrations of HCHO, the rate should be given by expression (i). Thus, a plot of $(d[CO]/dt)/[HCHO][O_2]$ against $[HCHO][O_2]$ should extrapolate to k_1 at zero $[HCHO][O_2]$. Determination of k_1 in this way over the temperature range 440 - 542.5°C gave the expression[34] $A_1 = 2.04 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $E_1 = 38.9$ kcal mol^{-1}. This represents one of the few direct determinations of Arrhenius parameters for the initiation process in hydrocarbon oxidation. Studies in vessels of 5.1 and 2.0 cm diameter confirmed that the initiation reaction was homogeneous.

To interpret the rate of reaction with HCHO concentrations of 1 Torr and above, the full mechanism involving reactions (1) - (8) must be treated using a computer treatment. Stationary state equations are written for the radicals HO_2, OH and HCO, and differential equations written for the formation of CO and of H_2O_2.

$$d[CO]/dt = -d[HCHO]/dt = k_1[HCHO][O_2] + k_3[HO_2][HCHO] + k_8[OH][HCHO]$$

$$d[H_2O_2]/dt = k_3[HO_2][HCHO] + k_5[HO_2]^2 - k_7[H_2O_2][M] - k_6[H_2O_2]$$

Step-wise integration, with a short time interval of 0.1 s, enables the progress of the reaction with time to be calculated and compared with the experimental results. The programme requires values of k_1, $k_3/k_5^{\frac{1}{2}}$, $k_4/k_5^{\frac{1}{2}}$ k_6 and k_7. k_7 has been independently determined, $k_3/k_5^{\frac{1}{2}}$ has been evaluated from a study[35] of the effect of HCHO on the induction period of $H_2 + O_2$ mixtures, and k_1 has been obtained in the present work. Adjustment of the values of $k_4/k_5^{\frac{1}{2}}$ and k_6 to give minimum deviation between observed and calculated CO, time profiles, for a wide range of mixtures, gives a value of k_4 in agreement with that calculated by assuming diffusion control, but k_6 is found to be only about one-quarter of the diffusion-controlled value. k_4 can thus be expressed by equation (iv) for an efficient surface, whereas k_6 requires the expression (v) for a moderately efficient surface.

$$k_4 = aA_4/P \qquad \text{(iv)}$$

$$k_6 = aA_8/P(1 + 4aB/P) \qquad \text{(v)}$$

a is close to unity, and expresses the diffusion coefficient of the mixture relative to N_2 as unity. B is given by $8\lambda_o/\epsilon d$, where ϵ is the surface efficiency, λ_o is the mean free path of H_2O_2 in N_2 at unit pressure, and d is the vessel diameter. Using these equations for k_4 and k_6, the optimisation procedure gives $A_7/k_5^{\frac{1}{2}} = 4.6$ $(Torr^3\ s^{-1})^{\frac{1}{2}}$ in close agreement with the calculated value from diffusion theory of 4.2, and the value of B is 161. This work has been published[34].

(b) The oxidation of acetaldehyde and propionaldehyde

The complexities involved in the oxidation of CH_3CHO were discussed at length in the previous report[14]. Some aspects of the experimental work have been repeated to confirm the main features of the reaction. A comprehensive mechanism has been written to interpret the results, and some progress has been made in the elucidation of the extremely complex mechanism of the oxidation of CH_3 radicals. Further work on this topic is desirable.

The main features of the oxidation of C_2H_5CHO were also presented in the previous report[14]. Recently, a detailed study of the yields of CO_2 has been carried out over a wide range of mixture composition, total pressure, and vessel diameter. As observed with $i\text{-}C_3H_7CHO$ (section 3c), the $[CO_2]/[CO]$ yields decrease with extent of reaction. The results are currently being analysed with the aid of a computer programme, and the mechanism is considered to be similar to that proposed for the formation of CO_2 in the oxidation of $i\text{-}C_3H_7CHO$.

(c) The oxidation of isobutyraldehyde and n-butyraldehyde

Studies of the oxidation of $i\text{-}C_3H_7CHO$ in aged boric-acid-coated vessels have been completed. The mechanism is similar to that proposed for the oxidation of C_2H_5CHO [14,36], and the system provides a reliable and controllable source of $i\text{-}C_3H_7$ and HO_2 radicals. An interesting feature of the effect of temperature is that, unlike the oxidation of most alkanes and related compounds, including aldehydes, where there is a well-defined region with a negative temperature coefficient, the rate of oxidation of $i\text{-}C_3H_7CHO$ increases almost continuously between 300 and 510°C, except for a possible slight decrease between 380 and 390°C.

The main study was carried out at 440°C over a wide range of mixture composition and total pressure. Propane, in trace amounts, and propene (ca. 75% yield) are the only primary hydrocarbon products formed, although CH_4 is formed in a secondary process. Propene and propane are formed in the competing reactions (1) and (2), so that the relative rate of formation is given by expression (vi)

$$d[C_3H_6]/d[C_3H_8] = k_9[O_2]/k_{10}[i\text{-}C_3H_7CHO] \qquad (vi)$$

The experimental results are consistent with the expression over a 30-fold range of $[O_2]/[i\text{-}C_3H_7CHO]$ and a 4-fold variation in total pressure, and a value of $k_9/k_{10} = 312 \pm 30$ at 440°C has been obtained. Use of the modified[37] literature value for k_{10} gives $k_9 = 1.3 \times 10^8$ dm^3 mol^{-1} s^{-1}, which may be compared with rate constants for similar reactions by reference to Table 5 (section 2b).

$$i\text{-}C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (9)$$

$$i\text{-}C_3H_7 + i\text{-}C_3H_7CHO = C_3H_8 + i\text{-}C_3H_7CO \qquad (10)$$

Addition of H_2 and D_2 increases the yield of propane due to the occurrence of reactions (11) and (12). From measurements of the increased yield, the values $k_9/k_{11} = 3060 \pm 250$ and $k_9/k_{12} = 7680 \pm 300$ at 440°C are obtained.

$$i\text{-}C_3H_7 + H_2 = C_3H_8 + H \qquad (11)$$

$$i\text{-}C_3H_7 + D_2 = C_3H_7D + D \qquad (12)$$

From k_9 above, the absolute values become $k_{11} = 4.15 \times 10^4$ and $k_{12} = 1.65 \times 10^4$ dm^3 mol^{-1} s^{-1}, and they are compared in Table 7 with the rate constants of the analogous reactions of CH_3, C_2H_5, and $n\text{-}C_3H_7$ radicals. A similar isotope effect is observed with all four alkyl radicals, and the variation of the rate constants is consistent with the change in the enthalpies of reaction. No independent data are available, but from the known value of k_{-11} (section 2a) and the best available thermochemistry of reaction (11), $E_{11} = 16.9$ kcal mol^{-1} and $A_{11} = 3.2 \times 10^9$ dm^3 mol^{-1} s^{-1} are recommended. This aspect of the work on the oxidation of $i\text{-}C_3H_7CHO$ has been published[37].

Table 7

Values of $k(R + H_2)$ and $k(R + D_2)$ at 440°C

R	$D(R - H)$/ kcal mol^{-1}	$k(R + H_2)$/ $dm^3\ mol^{-1}\ s^{-1}$	$k(R + D_2)$/ $dm^3\ mol^{-1}\ s^{-1}$	$\frac{k(R + H_2)}{k(R + D_2)}$
CH_3	104	6.05×10^5	2.75×10^5	2.2
C_2H_5	99	7.75×10^4	2.95×10^4	2.6
$n\text{-}C_3H_7$	100	4.50×10^4	1.95×10^4	2.3
$i\text{-}C_3H_7$	95.5	4.15×10^4	1.65×10^4	2.5

A computer programme has been written to follow the progress of the oxidation of $i\text{-}C_3H_7CHO$ with time using a Kutta-Runge integration procedure, and it is being currently used to interpret the yields that have been obtained for the various products over a range of reactant concentrations. The computer results indicate that the optimum values of the two parameters k_{13} and $k_{14}/k_{15}^{\frac{1}{2}}$, chosen so as to give the best interpretation of the $[C_3H_6]$, time relationships, are virtually independent of the values of the other rate constants used, over an acceptable range. The values of $k_{13} = 0.023\ dm^3\ mol^{-1}\ s^{-1}$ and $k_{14}/k_{15}^{\frac{1}{2}} = 48\ (dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$ at 440°C are consistent with the corresponding values obtained from studies of the oxidation of formaldehyde[34,35] and propionaldehyde[36], but may be modified slightly ($\pm$ 10%) by a more sophisticated treatment of the results.

$$i\text{-}C_3H_7CHO + O_2 = i\text{-}C_3H_7CO + HO_2 \quad (13)$$

$$HO_2 + i\text{-}C_3H_7CHO = H_2O_2 + i\text{-}C_3H_7CO \quad (14)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \quad (15)$$

The formation of CO_2 (yields ca. 5%) present a minor complication in the mechanism. The experimental ratio $[CO_2]/[CO]$ decreases considerably with time for all mixtures studied and also increases if a vessel of small diameter is used. This cannot be predicted by any mechanism involving only homogeneous reactions, and the simplest explanation is

that CO_2 is formed both in a molecular surface process and in the gas phase by a sequence such as

$$(CH_3)_2CHCO + O_2 \rightarrow (CH_3)_2CHCO_3 \longrightarrow \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_2 \end{matrix} CHCO_3H \rightarrow C_3H_6 + CO_2 + OH$$

As the homogeneous chain reaction is autocatalytic, CO_2 is formed relatively faster in the early stages, so that the ratio $[CO_2]/[CO]$ decreases with extent of reaction. After allowance for the surface formation of CO_2, rate constants can be obtained for the elementary reactions involved in the homogeneous process.

A similar study of the oxidation of $n\text{-}C_3H_7CHO$ has been made; the experimental results are discussed in the last report. A detailed mechanism has been developed to interpret the results, but the system is complicated by the presence of CH_3 radicals, which undergo radical-radical reactions and form CH_3OOH by the sequence

$$CH_3 + O_2 \rightarrow CH_3O_2 \xrightarrow{RCHO} CH_3OOH$$

A detailed treatment must therefore await a clearer understanding of the oxidative chemistry of the CH_3 radical than is currently available.

4. Decomposition of Hexamethylethane in the Presence of Oxygen

$$RH + O_2 = R + HO_2 \quad (0)$$

$$RH = R' + R'' \quad (1')$$

To complement existing methods of studying the elementary reactions involved in hydrocarbon oxidation, the decomposition of hexamethylethane (HME) has been examined as a possible source both of t-butyl radicals and of HO_2 radicals. For most hydrocarbons, the rate of the normal initiation reaction (0) is greater than the unimolecular decomposition (1') at temperatures below 500°C, as instanced by the sensitising effect of traces of oxygen on the pyrolysis of hydrocarbons. However, in the case of HME, calculations, using the Arrhenius parameters for k_1 given by Tsang[38], and a reasonable estimate of k_0 based on the corresponding Arrhenius parameters[24] for C_2H_6, show that the rate of reaction of HME with O_2, at pressures of O_2 up to 1 atmosphere, is about 1000 times slower than the decomposition of HME, in the temperature range 440 - 540°C. This is confirmed by the experimental observation that the rate of decomposition of HME is independent of O_2 concentration over a ten-fold range.

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

$$t\text{-}C_4H_9 + O_2 = (CH_3)_2C{=}CH_2 + HO_2 \quad (2)$$

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

$$HO_2 + HME = (CH_3)_3C\text{-}C(CH_3)_2CH_2 + H_2O_2 \quad (4)$$

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

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

$$H_2O_2 \xrightarrow{\text{surface}} H_2O + \tfrac{1}{2}O_2 \quad (7)$$

$$OH + HME = (CH_3)_3C\text{-}C(CH_3)_2CH_2 + H_2O \quad (8)$$

$$(CH_3)_3C\text{-}C(CH_3)_2CH_2 = (CH_3)_2C{=}CH_2 + t\text{-}C_4H_9 \quad (9)$$

The homogeneous decomposition is normally a chain process because of attack of the radicals R' and R'' on the parent material. This can be

avoided in the decomposition of HME by the addition of O_2, since 99% of t-butyl radicals undergo reaction (2) with O_2 to form isobutene and HO_2. At temperatures above about 440°C, dissociation of H_2O_2, formed by reactions (4) and (5) could become significant and produce hydroxyl radicals. Such interference can, however, be minimised by the use of a KCl-coated surface[34] which is highly efficient for the destruction of HO_2, and reasonably efficient for the destruction of H_2O_2.

The simplest mechanism for the decomposition of HME in the presence of O_2 thus involves reactions (1) - (3), and this gives relationship (i) between loss of HME ($\Delta[HME]$), pressure change (ΔP), and isobutene formation ($[IB]$), and the kinetic expression shown in equation (ii).

$$\Delta[HME] = {}^{2}/_{3}\Delta P = \tfrac{1}{2}[IB] \qquad \text{(i)}$$

$$-d[HME]/dt = k_1[HME] \qquad \text{(ii)}$$

Analysis confirms the validity of equation (i) in the early stages of reaction; as the reaction proceeds the system becomes more complex due to reactions of the product, isobutene. The mechanism involving (1) - (3) predicts isobutene as the sole product; analysis shows that the yield is about 98%, together with about 1% of isobutene oxide and of isobutane. The former product is formed by reaction of t-butyl radicals with O_2 and will be discussed later. Isobutane is believed to be formed in a direct molecular reaction which is currently under investigation.

The kinetic results are entirely consistent with expression (ii), the initial rate being independent of the concentration of O_2 over a ten-fold range, and almost exactly first order in HME. The value of the rate constant k_1, calculated from expression (ii), does increase slightly (ca. 15%) with increasing HME concentration over the range 0.5 - 4 Torr, and also increases on addition of N_2. This is due to a very small contribution from a chain process, resulting from reactions (4) - (9), the HO_2 attack on HME being the more important process at low pressures and low temperatures, whereas OH + HME becomes increasingly important as the pressure and temperature are increased. It is believed that the increase in k_1 will allow the evaluation of $k_4/k_5^{\frac{1}{2}}$, and a preliminary value of 0.36 $(dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$ has been obtained. Since $k_5 = 2 \times 10^9$, $k_4 = 1.6 \times 10^4$ $dm^3\ mol^{-1}\ s^{-1}$ at 440°C.

Table 8

Summary of results

T/°C	k_1/s^{-1} (for HME ≤1 Torr)	(k_1/s^{-1}) (corrected)
440.0	2.82×10^{-5}	2.70×10^{-5}
470.0	2.38×10^{-4}	2.11×10^{-4}
500.0	1.48×10^{-3}	1.37×10^{-3}
520.0	4.62×10^{-3}	4.17×10^{-3}
542.0	1.52×10^{-2}	1.38×10^{-2}

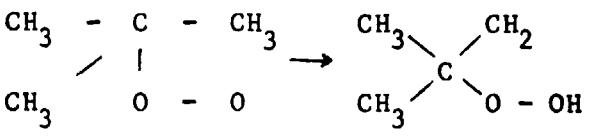
The values of k_1, corrected for this small chain contribution, are shown in Table 8, together with the uncorrected values. The log k_1(corrected), 1/T plot gives an excellent straight line with $A = 1.20 \times 10^{17}$ s^{-1}, $E = 70.6$ kcal mol^{-1}. If the present values of k_1 are combined with those obtained by Tsang[38] over the temperature range 985 - 1141 K using a shock-tube technique, the corresponding Arrhenius parameters are $A = 6.0 \times 10^{16}$ s^{-1}, $E = 69.4$ kcal mol^{-1}.

By combining the rate constant for reaction (1) at various temperatures with those for the reverse reaction, the enthalpy and entropy changes in the reaction, and hence the standard enthalpy and entropy of formation of t-butyl radicals at 298 K, can be calculated. The exact value depends on (a) whether k_{-1} is independent of temperature, or has a small negative temperature coefficient, as some experimental measurements[39] suggest, (b) the barrier assumed for internal rotation in the t-butyl radical, which affects the conversion of the values at the experimental temperature to those at 298 K. Both the present result for k_1 alone, and that obtained from combination with Tsang's determination, give effectively identical values of $\Delta_f H^\circ_{298}$(t-Bu) and S°_{298}(t-Bu). If a rotational energy barrier of 2 kcal mol^{-1} is assumed, and if k_{-1} is assumed to be independent of temperature, S°_{298}(t-Bu) = 72.8 cal mol^{-1} K^{-1}, $\Delta_f H^\circ_{298}$(t-Bu) = 10.5 kcal mol^{-1}. If the experimental temperature dependence is accepted, S°_{298}(t-Bu) = 74.9 cal mol^{-1} K^{-1}, $\Delta_f H^\circ_{298}$(t-Bu) = 11.6 kcal mol^{-1}. The lower of the two values of $\Delta_f H^\circ_{298}$ implies a bond

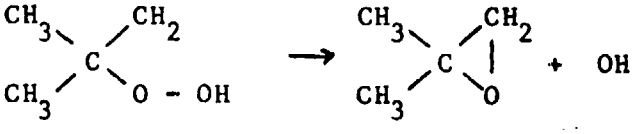
dissociation energy D^{o}_{298}(t-Bu-H) of 95.0 kcal mol^{-1}, which is some 2.5 kcal mol^{-1} higher than the currently proposed value.

Measurements of the initial yields of isobutene and isobutene oxide show that the ratio of these products is independent of the concentrations of O_2 and HME, and decreases slightly as the temperature rises, corresponding to an activation energy of -3 kcal mol^{-1}. It is now accepted that isobutene oxide is formed by the P.R.I.D. (peroxy-radical isomerisation and decomposition) mechanism, summarised below.

$$t\text{-}C_4H_9 + O_2 \rightleftharpoons t\text{-}C_4H_9O_2 \qquad (10)$$



(11)



(12)

Since reaction (10) is effectively equilibrated

$$d[C_4H_8]/d[C_4H_8O] = k_2/K_{10}k_{11} \qquad (iii)$$

From the experimental ratio of 105 at 500°C, and the calculated value of K_{10} = 88 dm^3 mol^{-1}, k_2/k_{11} = 9220 dm^3 mol^{-1}. From a reasonable estimate (section 2b) of k_{11} = 3.7 x 10^3 s^{-1} for similar reactions, k_2 = 3.4 x 10^7 dm^3 mol^{-1} s^{-1}, consistent with values given in Table 4 of section (2) for other alkyl radicals. From the observed activation energy, of -3 kcal mole, ΔH_{10} = 27 kcal mol^{-1} and E_2 = 5 kcal mol^{-1}, a value of E_{11} = 35 ± 3 kcal mol^{-1} is obtained, in good agreement with the value suggested in Table 5 for a 1,4p transfer.

This work has been submitted for publication. It is planned to continue studies of the decomposition of hexamethylethane to examine its potential as a source of t-butyl radicals and of HO_2 radicals.

5. The Reaction between Hydrogen and Nitrous Oxide

Although this reaction has been studied by a number of workers[40-45], the detailed mechanism still remains uncertain. The basic mechanism clearly involves the chain propagation steps (3) and (4) listed below, and the reaction thus offers a possible controlled source of H atoms and OH radicals at temperatures significantly higher than the range 460 - 520°C over which the $H_2 + O_2$ reaction can conveniently be used in the manner described in section (2).

$$H + O_2 = OH + O \qquad (a)$$

To reduce the number of unknown rate constants, reaction (3) was studied independently by the addition of N_2O to slowly reacting mixtures of $H_2 + O_2 + He$. From measurements of the relative rate of production of N_2 and H_2O, the ratio of the rate constants $k_3/k_a = 0.64 \pm 0.07$ was obtained at 500°C. This work was described in an earlier report[14], and has now been published[46]. At that time, the best procedure was to use the recommended value[5] of $k_a = 2.24 \times 10^{11} \exp(-8450/T)$ to obtain $k_3 = 2.6 \times 10^6$ dm^3 mol^{-1} s^{-1} at 500°C. Combination[46] with values obtained by other workers gave the Arrhenius parameters $A_3 = 7.6 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $E_3 = 15.1 \pm 1.0$ kcal mol^{-1}. However, the value of k_a is uncertain to about ± 30% around 500°C, and a more accurate evaluation of k_a at 500°C can probably be made by combining the ratio* $k_b/k_a = 38.6$ at 500°C with the independent determination[17] of $k_b = 2.96 \times 10^8$ to give $k_a = 7.67 \times 10^6$ at 500°C, so that $k_3 = 4.9 \times 10^6$ dm^3 mol^{-1} s^{-1}.

$$H + C_2H_6 = H_2 + C_2H_5 \qquad (b)$$

Since this work was completed, Behring, Hoyermann, Schacke and Wolfrum[48] have used a flow discharge method to obtain the Arrhenius parameters $A_3 = 1.3 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, $E_3 = 16.0$ kcal mol^{-1}. These give $k_{22} = 3.9 \times 10^6$ at 500°C, in excellent agreement with the present value. A later paper by the same authors, with Albers and Schmatyko[49] gives $A_3 = 2.2 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, $E_3 = 17.3$ kcal mol^{-1}, from which

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* This value is based on studies of the addition of C_2H_6 to slowly reacting mixtures of $H_2 + O_2 + N_2$; the original data[47] have been re-interpreted as described in section (2a).

$k_3 = 2.8 \times 10^6$ dm^3 mol^{-1} s^{-1}.

N_2O	+	M	=	N_2	+	O	+	M	(1)
O	+	H_2	=	OH	+	H			(2)
H	+	N_2O	=	OH	+	N_2			(3)
OH	+	H_2	=	H	+	H_2O			(4)
H			surface =			$\frac{1}{2}H_2$			(5)
H	+	H	+ M =	H_2	+	M			(6)
H	+	N_2O	=	NH	+	NO			(7)
NH	+	N_2O	=	HNO	+	N_2			(8)
H	+	HNO	=	H_2	+	NO			(9)
OH	+	HNO	=	H_2O	+	NO			(10)
H	+	NO	+ M' =	HNO	+	M'			(11)
HNO	+	HNO	=	H_2O	+	N_2O			(12)
HNO	+	M'	=	H	+	NO	+	M'	(13)
HNO	+	NO	=	OH	+	N_2O			(14)

The reaction between H_2 and N_2O was studied at 540°C, and in detail at 600°C. Since the overall reaction $H_2 + N_2O = N_2 + H_2O$ involves no pressure change, the reaction was followed by measurement of the N_2 produced over a range of H_2 and N_2O concentrations, total pressure and inert gas (He) addition.

The simplest mechanism involves initiation by reactions (1) and (2), and propagation by reactions (3) and (4). The only obvious termination reactions are (5) and (6). The surface termination process (5) can be excluded on two grounds. First, the rate was found to be identical in aged boric-acid-coated vessels, in silica vessels, and in pyrex vessels, despite the fact that the efficiency of destruction of H atoms at these surfaces is known to vary considerably. Secondly, from the known value of k_1 and the observed rate, the chain length is about 100 for $[N_2O] = [H_2] = 100$ Torr at 540°C; since the chain length

would be $k_3[N_2O]/k_5$, the known value of $k_3 = 7.08 \times 10^6$ at 540°C would require $k_5 = 100\ s^{-1}$, which is at least ten times the maximum possible (diffusion-controlled) value, and very much greater than the actual value.

Chain termination by reaction (6) would give an order of 1.5 in N_2O, close to the experimental value of 1.2. However, for long chains,

$$d[N_2]/dt = k_3[H][N_2O] \qquad (i)$$

Use of this equation to calculate [H] shows that the rate of (6) is less than 0.01% of the rate of initiation by reaction (1) at 540°C.

The only feasible alternative chain termination process appears to be reaction (7). A mechanism involving reactions (1) - (4) and (7) gives the rate expression (ii) if it is assumed that all NH radicals undergo termination reactions.

$$d[N_2]/dt = 2k_1k_6[N_2O][M]/k_7 \qquad (ii)$$

This predicts zero order in H_2 and near unity in N_2O (since [M] may change with $[N_2O]$ at constant pressure if N_2O and He have different efficiencies in reaction (1)), consistent with the experimental results using initial rates. The integrated rate relationship, however, indicates an order greater than two; this suggests that the reaction is self-inhibiting, due to the NO formed in reaction (7), which removes H atoms by reaction (11). Tests with added NO confirmed that there was a marked inhibiting effect even at concentrations as low as 0.1 Torr. To measure such low concentrations of NO in reacting mixtures, the Saltzmann[50] colorimetric method was used. These measurements showed that the concentration of NO rose rapidly in the early stages of reaction (thus accounting for the marked self-inhibition) but reached a flat maximum and then gradually decreased.

The most likely reaction of the NH radicals formed in (7) is the highly exothermic process (8). Reactions (9) - (14) are possible reactions of HNO radicals, of which (10) will be unimportant because of the high rate of reaction (4) at all H_2 concentrations used. In considering the importance of the remaining reactions of NO, the following points have to be taken into account.

(a) The markedly inhibiting effect of NO at very low concentration decreases sharply as the NO concentration is increased, and the rate is only decreased slightly as the NO concentration is increased from 1 to 5 Torr as indicated in Table 9 below.

Table 9

Inhibiting effect of NO on $N_2O + H_2$ reaction

$N_2O = H_2 = 100$ Torr; total pressure 500 Torr; temperature 600°C

$[NO]$/Torr	0	0.1	0.2	0.5	1.0	2.5	5
Rate/(Torr s^{-1})	0.0635	0.377	0.26	0.140	0.092	0.063	0.045

This decrease in the inhibiting effect of NO at high concentrations of NO can only be explained by introducing reaction (14).

(b) The termination reaction (9) converts HNO formed by reactions (7) and (8), and by (11), back into NO, so that $\Delta[NO]/\Delta[N_2]$ would remain constant throughout the reaction, and equal $2k_7/k_3$, if (9) was the sole termination process. Experimentally, the NO concentration rises to a maximum of about 0.1 Torr and then decreases as the reaction proceeds.

(c) If all HNO radicals undergo the termination reaction (12), the chain length is k_3/k_7 and estimates of about 150 for this ratio can be obtained from the initial value of $\Delta[NO]/\Delta[N_2]$. Calculation of the chain length from the initial reaction rate and the initiation rate $2k_1[N_2O][M]$ is uncertain, partly because of discrepancies in the published values of k_1 and partly because of the uncertain coefficients for H_2 and He relative to N_2O in reaction (1). The values suggest that while the fraction of HNO radicals undergoing termination is likely to be close to unity, the possibility that it is significantly less than unity, as a consequence of reaction (13), cannot be excluded.

For a detailed interpretation using a mechanism involving reactions (1) - (4) and (7) - (14), a computer treatment is necessary. Because of the unknown coefficients of H_2 and He relative to those of N_2O in reactions (1), (7), and (8), detailed attention has concentrated on the interpretation of two types of measurement:

(a) the inhibiting effect, on the initial rate, of addition of NO in the concentration range 0-5 Torr to a standard mixture (N_2O = 100 Torr, H_2O = 100 Torr, He = 300 Torr),

(b) the [NO], time profile for this mixture.

Neglecting reaction (10), the computer programme contains seven unknown parameters, k_1, k_7/k_3, k_{11}/k_3, k_9/k_3, k_{12}, k_{13}, and k_{14}. An optimisation procedure was incorporated into the computer programme, and it was found that a significant optimisation could be achieved for up to five of these parameters, namely k_1, k_7/k_3, k_{11}/k_3, k_{12}, and k_{14}. However, effectively the same r.m.s. deviation between observed and calculated values (4% for the initial rate of 10 mixtures, 3% for the NO profile at 8 different times) could be obtained over a wide (at least 16-fold) range of k_9/k_3 with k_{13} = 0, or a similar range of k_{13} with k_9/k_3 = 0, or with combinations of k_9/k_3 and k_{13}. With k_{13} = 0, the values of k_1, k_7/k_3 and k_{11}/k_3 were independent of k_9/k_3 whereas k_{14} increased proportionally to k_9/k_3, and k_{12} proportionally to $(k_9/k_3)^2$. When k_{13} was varied with k_9/k_3 = 0, k_1, k_7/k_3 and k_{11}/k_3 were similarly constant, but at slightly different values, whereas k_{14} increased proportionally to k_{13}, and k_{12} proportionally to k_{13}^2. It thus appears impossible to obtain a unique solution from the present experimental observations, although three of the parameters can be defined with reasonable accuracy at 600°C, namely $k_1 = (2.6 \pm 0.7) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} (M = N_2O), $k_7/k_3 = (4.1 \pm 0.5) \times 10^{-3}$, $k_{11}/k_3 = 480 \pm 30$ dm^3 mol^{-1}. This work has now been published[51].

Two approaches have recently been made in an attempt to resolve the present deadlock in the further elucidation of the rate constants involved.

(a) A very wide range of mixtures of H_2 + N_2O + He has been taken, including mixtures without added NO, and mixtures with added NO, and the computer has been used to predict the initial reaction rates for a wide range of the different sets of parameters that have been found to interpret accurately the experimental data indicated earlier. In particular, high and low values of k_8 with k_9 = 0, high and low values of k_9 with k_{13} = 0, and several combinations of k_9 and k_{13}, have been taken; in each case the optimum set of the remaining parameters

k_1, k_7/k_3, k_{11}/k_3, k_{12}, and k_{14} has been used. The calculations show that the rates are remarkably insensitive to the particular set of parameters used and do not offer any encouragement for the hope that a specific set of parameters can be located by further experimental work, particularly in view of the further difficulty of the uncertain coefficients for N_2O, H_2 and He in reactions (1), (7) and (8).

(b) At the same time, the effect of different inert gases in the reaction has been studied by examining the effect of Ar, He, CO_2, and H_2O on the rate of the reaction between H_2 and N_2O. H_2O is a product and, as the reaction proceeds, becomes an important contributor to $[M]$. Results with CO_2 are of interest in view of the projected use of the system as a source of OH radicals to study their reaction with CO. Most of the results have been obtained with the mixture containing 25 Torr of N_2O and of H_2, so that the effect of added inert gas is relatively high. Separate addition of 450 Torr of He, Ar, and CO_2 increases the initial rate by 65%, 35%, and 55%, respectively. Addition of 18 Torr of H_2O to the basic mixture increases the initial rate by about 30%. Interpretation of these results is being carried out by using a computer programme.

The reaction between H_2 and N_2O has also been studied at 500°C by an alternative method involving direct sampling from the reaction vessel into a mass spectrometer, and measurement of the N_2 formed. The most satisfactory form of leak was a needle valve located just outside the reaction vessel, which gave a time lag of about 5 seconds with the pressures used, compared to reaction times of several minutes. The reaction has been studied in aged boric-acid-coated vessels, in pyrex vessels, and in vessels freshly coated with boric acid, and no effect of vessel surface was observed. Argon has been used as internal standard for the mass spectrometer, and the observed rates are identical with those found using gas chromatography to determine the N_2 production.

The rate of reaction is independent of H_2 pressure, and increases only very slightly when argon is added up to pressure of 300 Torr to the basic mixture of H_2 and N_2O, each at a pressure of 100 Torr. Plots of log(initial rate) against log(N_2O) give an order of 1.2 in N_2O, but the fall-off in rate during a reaction is consistent with an order of nearly three. As mentioned above, this apparent discrepancy is due to inhibition by nitric oxide, formed in reaction (7), and experiments

have been carried out to estimate quantitatively the NO formed. Experiments to determine the effect of NO at 500°C by studying the reaction in the presence of NO have also been carried out. The results are being examined by the use of the computer programme, and it is hoped to obtain rate constants for some of the elementary steps for comparison with the values available at 600°C.

An attempt has been made to study the reaction of CO with OH radicals by adding CO to reacting H_2 + N_2O mixtures. If CO_2 is solely formed by reaction (15), and N_2 solely by reaction (3), then the relative rate of formation of CO_2 and N_2 is given by equation (iii).

$$OH + CO = CO_2 + H \qquad (15)$$

$$d[CO_2]/d[N_2] = k_{15}[CO]/k_3[H_2] \qquad (iii)$$

As a necessary preliminary, the decomposition of N_2O in the presence of CO has been studied to ensure that there is no direct molecular or surface reaction between N_2O and CO.

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"The second limit of hydrogen + carbon monoxide + oxygen mixtures".

2. R. R. Baldwin, A. Gethin, and R. W. Walker.
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"Reaction of hydrogen atoms with nitrous oxide".

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"Activation energies of hydrogen atom abstractions from alkanes by free radicals".

6. R. R. Baldwin and R. W. Walker.
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"The role of radical-radical reactions in hydrocarbon oxidation".

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"The oxidation of formaldehyde as a source of HO_2 radicals".

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"Addition of n-C_4H_{10} and C_4H_8 to slowly reacting mixtures of hydrogen and oxygen at 480°C. Part 1. Formation of hydrocarbon products".

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Combustion and Flame, 1975, 25, 285.
"The addition of neopentane to slowly reacting mixtures of hydrogen and oxygen at 480°C. I. Formation of primary products from neopentane".

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"Addition of neopentane to slowly reacting mixtures of $H_2 + O_2$ at 480°C. II. The addition of the primary products from neopentane, and the rate constants for H and OH attack on neopentane".

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"Rate constants for reactions in gas-phase hydrocarbon oxidation".

18. R. R. Baldwin, Mrs. J. P. Bennett, and R. W. Walker.
Sixteenth Symposium (International) on Combustion, the Combustion Institute, Pittsburgh, 1977.
"Rate constants for elementary steps in hydrocarbon oxidation", in the press.

19. G. M. Atri, R. R. Baldwin, D. Jackson, and R. W. Walker.
Paper accepted for publication by Combustion and Flame.
"The reaction of OH radicals and HO_2 radicals with carbon monoxide".

20. R. R. Baldwin, J. C. Plaistowe, and R. W. Walker.
Paper accepted for publication by Combustion and Flame.
"The mechanism of conjugate alkene formation and the importance of surface reactions in hydrocarbon oxidation".

Conferences attended and Lectures presented

Professor Baldwin gave a colloquium at Cambridge University in 1973 entitled "The use of the high temperature oxidation of aldehydes to study the reactions of free radicals".

Dr. Walker gave a colloquium at York University in 1973 on the determination of velocity constants by the use of the hydrogen + oxygen reaction.

Professor Baldwin and Dr. Walker attended the 1973 European Combustion Symposium at Sheffield, and presented a paper entitled "The oxidation of formaldehyde as a source of HO_2 radicals".

Dr. Walker attended the 14th U.S.A.F. Contractors' Meeting on "The kinetics of energy conversion" held at Boston College in 1973, and gave a talk entitled "The oxidation of formaldehyde in potassium-chloride-coated vessels".

Professor Baldwin and Dr. Walker gave a paper entitled "Rate constants in hydrocarbon oxidation" at a meeting of the British Section of the Combustion Institute held at the University of Liverpool in 1974. The subject of the meeting was "Mechanisms of combustion processes".

Professor Baldwin and Dr. Walker attended a one-day research meeting on "Combustion" at the University of York in 1974.

Professor Baldwin attended the 1974 U.S.A.F. Combustion Kinetics Meeting at the University of California, Berkeley, and gave a talk on "The reaction between hydrogen and nitrous oxide".

Professor Baldwin gave an invited seminar at the Statewide Air Pollution Research Centre, University of California, Riverside, entitled "The elementary reactions involved in the oxidation of hydrocarbons and related compounds".

Professor Baldwin and Dr. Walker gave the Schools Christmas Lecture entitled "Combustion - some burning problems", to some five hundred Hull pupils on two successive evenings.

In 1975, Professor Baldwin gave an invited lecture entitled "Problems and progress in the gas phase oxidation of hydrocarbons" at the Fourth International Symposium on Gas Kinetics, held at Heriot-Watt University, Edinburgh.

Dr. Walker attended the 1975 U.S.A.F. Combustion Kinetics Contractors' Meeting at Eglin Air Force Base, Florida, and gave a talk entitled "The mechanism of product formation in the oxidation of hydrocarbons".

Conferences attended and Lectures presented / continued

Dr. Walker attended the Sixteenth International Combustion Symposium held at Boston, Massachusetts in 1976, and presented a paper entitled "Rate constants for elementary steps in hydrocarbon oxidation".

Dr. Walker was invited to attend a three-day symposium held in August 1976 at the U.S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland, and gave two talks entitled "A critical survey of rate constants in combustion reactions" and "The high temperature oxidation of aldehydes".

Dr. Walker visited N.A.S.A., Cleveland, in August 1976, and gave a talk on "Problems and progress in hydrocarbon oxidation".

Professor Baldwin and Dr. Walker attended a one-day meeting on "Recent advances in gas-phase combustion" at the University of Liverpool in 1976.

Professor Baldwin gave a lecture at Leeds University in May 1976 on "The mechanism of hydrocarbon oxidation".

Professor Baldwin attended the 1977 U.S.A.F. Contractors' Meeting on "Combustion and Plume Kinetics" held at the Arnold Engineering Development Center, Arnold Air Force Station, Tullahoma, Tennessee, and gave a talk entitled "The oxidation of hexamethylethane as a source of t-butyl radicals".

Personnel

Dr. K. A. Lewis, who was financed by a Science Research Council award from 1969 - 1972, has successfully submitted for the Ph.D. degree. He is now employed in the Computer Department, University of Surrey.

Dr. A. Gethin, who was supported under Grants AF EOOAR 68-0013 and AFOSR 73-2450 from 1970 - 1973, has successfully submitted for the Ph.D. degree. He is now employed at British Nuclear Fuels, Preston.

Dr. A. R. Fuller, who was financed under Grants AF EOOAR 68-0013 and AFOSR 73-2450 from 1970 - 1973, has successfully submitted for the Ph.D. degree. After a period at the Computing Laboratory at Oxford University, he has now taken up a position with I.C.L.

Mrs. M. E. Fuller, a University-financed technician from 1970 - 1973, was employed at the Dyson Perrins Laboratory, Oxford University, until recently.

Mr. C. J. Claugh and Mrs. J. P. Bennett, financed under Grant AFOSR 73-2450, have completed their period of study and will be submitting their theses shortly.

Mr. J. C. Plaistowe, a University-financed technician from 1973 - 1977, has recently resigned to take up an appointment in local industry as a chemist.

Mr. R. W. Walker (B.Sc., Hull 1975), financed by a Science Research Council award, joined the group in September 1975.

Mr. G. A. Evans (B.Sc., C.N.A.A., 1975) and Mr. M. Kyle (M.Sc., Leeds 1975) have joined the research group and are financed by Grant AFOSR 73-2450.

Informal discussions have taken place with Dr. Barnard of University College London, Professor Ashmore, Dr. Tyler and Dr. Simmons of the University of Manchester Institute of Science and Technology, Dr. Skirrow and Dr. Tipper of Liverpool University, Dr. Knox of Edinburgh University, Professor Gray, Dr. Williams, Dr. Dixon-Lewis, and Dr. Griffiths of Leeds University, Dr. Booth of Rutherford College of Technology, Dr. Quinn, Dr. Halstead, Dr. Luckett, and Dr. Parkes of the Thornton Research Centre, Dr. Brokaw and Dr. Brabbs of the National Aeronautics and Space Administration Lewis Research Centre at Cleveland, Dr. Pitts and Dr. Lloyd of the Riverside Research Centre, Dr. Golden of the Stanford Research Institute, Dr. Benson of the University of Southern California, and Dr. Cohen, of the Army Ballistic Missile Laboratory, Aberdeen Proving Ground.