

Decomposition of 4,4-Dimethylpent-1-ene in the Presence of Oxygen between 400 and 500°C: Oxidation Chemistry of Allyl Radicals

Zulfiqar H. Lodhi and Raymond W. Walker*

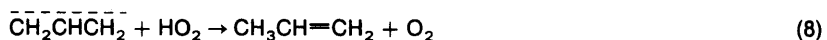
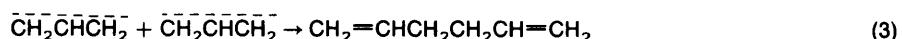
School of Chemistry, Hull University, Hull, N. Humberside, HU6 7RX, UK

The decomposition of 4,4-dimethylpent-1-ene (DMP) in the presence of O₂ has been used as a source of allyl radicals over the temperature range 400–500°C. The reaction has been studied in both KCl-coated (peroxy species destroyed at the surface) and aged boric-acid-coated vessels (peroxy species preserved), and the basic mechanism shown to be:



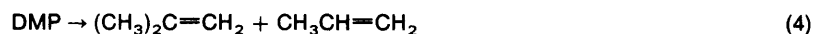
Previous studies have shown that 99% of the t-butyl radicals undergo reaction (2), so that the system is an excellent source of allyl and HO₂ radicals.

A full product analysis has been carried out over a wide range of mixture composition and associated mechanistic aspects discussed. It is shown that allyl radicals are unreactive towards both DMP and O₂ and that they react mainly in radical-radical processes.



Values of $k_8/k_{18} = 0.37$, 0.38 and 0.42 are obtained at 400, 440 and 480°C, respectively. From a reasonably reliable estimate of [HO₂] and [allyl], values of $k_8 = (3.3 \pm 0.9) \times 10^9$ and $k_{18} = (7.4 \pm 2.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ are obtained at 480°C. No previous estimates of these rate constants are available in the literature.

Values of k_4 have been determined and when combined with independent data at higher temperatures give $\log(A_4/s^{-1}) = 14.19 \pm 0.25$ and $E_4 = 255.5 \pm 5.3 \text{ kJ mol}^{-1}$ over the range 400–1025°C.



A value of $k_{11} = (2.5 \pm 1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been obtained at 480°C and shown to be consistent with the reaction's high endothermicity.

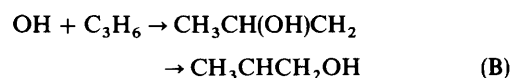


Success in modelling the many practical combustion problems where comprehensive oxidation mechanisms are used is markedly dependent on both the quantity and the quality of the data available on the elementary reactions involved. For each step, the data should include information on pathways and mechanism as well as rate constants. As temperature coefficients and in many cases pressure effects are required, the data requirement is potentially formidable.^{1,2} Whilst the quality of the kinetic data for key elementary reactions involving directly alkanes and alkyl radicals is far from satisfactory, the data base for alkenes and alkenyl radicals is vastly inferior.³⁻⁵ This deficiency is of great concern because, under many conditions, particularly in the autoignition region, alkenes are major initial products arising from the oxidation of alkanes; for example with 0.5 atm of oxygen, 99% of ethyl⁶ and t-butyl⁷ radicals, 80% of propyl⁸ radicals and 70% of butyl⁹ radicals (primary and secondary) give the appropriate conjugate alkene.

The double bond in alkenes exerts the dominant influence in determining oxidation behaviour, which is of enhanced complexity because both addition and abstraction reactions occur. Addition may give (particularly for lower alkenes) vibrationally excited radicals, such as in reaction (A), whose properties may differ considerably from those of the thermalised radical.

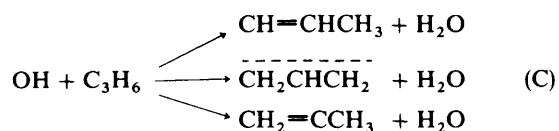


With $\Delta H_A \approx -160 \text{ kJ mol}^{-1}$, the $\text{CH}_3\text{CH}_2\text{CH}_2^*$ radical will undergo homolysis to $\text{CH}_3 + \text{C}_2\text{H}_4$ at much lower temperatures than the thermalised radical. For asymmetric alkenes addition of a radical gives two adducts such as in the very important process (B).



The further reactions of the hydroxy adducts in the presence of O₂ at combustion temperatures are far from fully elucidated.

H-atom abstraction by a non-selective radical may occur at any C—H bond in the alkene, as at the three positions in propene, but for a selective radical such as HO₂ abstraction will occur almost uniquely at the allylic position due to the low C—H bond dissociation energy.



As Table 1 shows, the bond-dissociation energies of allylic C—H bonds are considerably lower than those of other C—H bonds in alkanes and alkenes, the low values arising from electron delocalisation in the emerging allyl-type

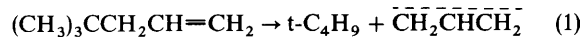
Table 1 C—H Bond-dissociation energies in alkanes and alkenes

bond	$D_0/\text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{—H}$	420
$(\text{CH}_3)_2\text{CH—H}$	402
$(\text{CH}_3)_3\text{C—H}$	390
$\text{CH}_2=\text{CHCH}_2\text{—H}$	363
$\text{CH}_3\text{CH}=\text{CH—H}$	460
$\text{CH}_3(\text{C—H})=\text{CH}_2$	445
$\text{CH}_2=\text{CH}(\text{CH—H})\text{CH}_3$	350
$\text{CH}_2=\text{CH}(\text{CH—H})\text{CH}_2\text{CH}_3$	350

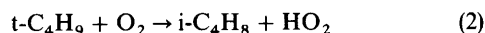
alkenyl radicals. The consequent enhanced stability of the alkenyl radicals plays a major role in the oxidation chemistry of alkenes. In a wider context, H-atom abstraction from the side chain in an alkylbenzene will give radicals stabilised by delocalisation into the benzene ring, for example, benzyl from toluene and PhCHCH_3 from ethylbenzene.

Little is known about the oxidation chemistry of any of these 'stable' radicals, and virtually no kinetic information is available on any of the elementary reactions involved.

In this paper, the oxidation chemistry of the prototypical stable alkenyl radical CH_2CHCH_2 will be examined. A good source of the radical is essential, and following the success^{10,11} of the decomposition of tetramethylbutane in the presence of O_2 as a source of t-butyl and HO_2 radicals, the decomposition of 4,4-dimethylpent-1-ene (DMP) has been used. By use of a competitive shock-tube technique, Tsang¹² obtained Arrhenius parameters of $10^{15.8} \text{ s}^{-1}$ and $E = 275 \text{ kJ mol}^{-1}$ for the homolysis step (1).



E_1 is relatively low (cf. 345 kJ mol^{-1} for $\text{C}_4\text{H}_{10} \rightarrow 2\text{C}_2\text{H}_5$), first because of the strain energy in the C—C bond between the two groups and secondly because of the electron delocalisation energy in the emerging allyl radical. At ca. 500°C in the presence of O_2 , 99% of t-butyl radicals react⁷ to form isobutene and HO_2 , so that the system provides an excellent source of allyl and HO_2 radicals.



Experimental

Unless specified, reactions were carried out in cylindrical Pyrex vessels, 20 cm in length and 5.2 cm i.d. coated either with KCl (fresh each week) or with boric acid. The boric-acid-coated vessels were aged to a well established condition¹³ by carrying out repeated reactions with $\text{H}_2\text{—O}_2$ mixtures. Pressure changes and absolute pressures < 50 Torr were measured by use of a Southern Electronic SE 180 pressure transducer, capable of an output of 1 mV for a pressure difference of 1 Torr. Electronically controlled solenoid valves were used to admit gases to the reaction vessel and to take samples at preset times. With a response time of ca. 0.1 s, precise admission and sampling times were achieved. With the exception of HCHO, determined colorimetrically, product analysis was carried out by gas chromatography. CO was determined by use of a Carlo-Erba instrument which incorporated a helium-ionisation detector. The detector had a non-linear response, so that extra care was necessary during the daily calibrations.

Results

The decomposition of DMP in the presence of O_2 has been studied at 400, 440, 480 and 500°C in KCl-coated and in aged boric-acid-coated vessels, mostly at a total pressure of

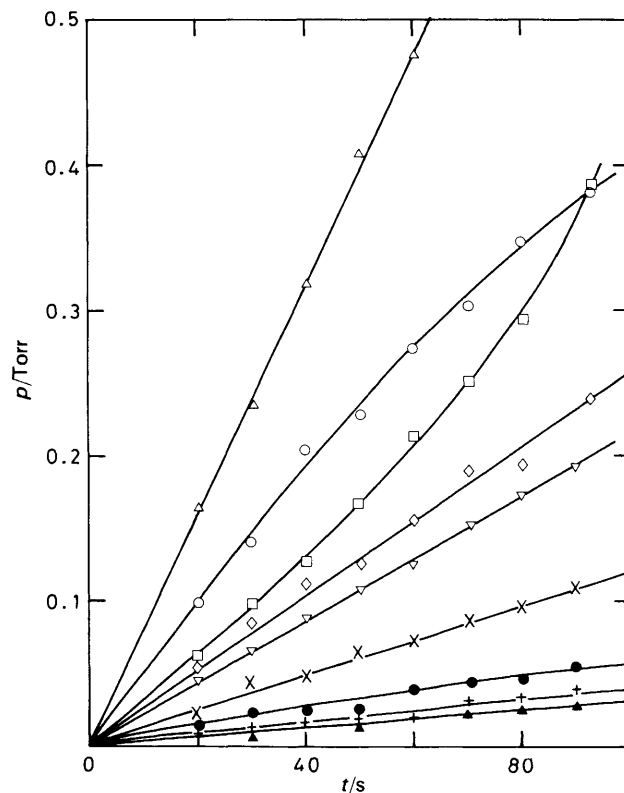


Fig. 1 Product yields in a 5.2 cm diameter KCl-coated vessel at 480°C . DMP = 4, $\text{O}_2 = 30$, $\text{N}_2 = 26$ Torr. Δ , isobutene; \circ , hexa-1,5-diene ($\times 10$); \square , CO; \diamond , HCHO; ∇ , C_3H_6 ; \times , C_2H_4 ; \bullet , acrolein; $+$, 4-methylpenta-1,3-diene; \blacktriangle , CH_4

60 Torr. The pressures of DMP and O_2 have been varied over the range 0.5–10 and 3–56 Torr, respectively, by exchange with N_2 . Pressure changes due to reaction were recorded, since they offered an 'instant' check on reproducibility. However, attention was focused mainly on the initial products of reaction (< 5% consumption of DMP). Fig. 1 shows the initial product profiles for the mixture containing 4, 30 and 26 Torr of DMP, O_2 and N_2 , respectively, at 480°C when the KCl-coated vessel is used. Isobutene is the major initial product, as expected from the mechanism, and CO, HCHO, C_3H_6 , hexa-1,5-diene (HDE), acetone, acrolein, C_2H_4 , CH_4 , and 4-methylpenta-1,3-diene are also observed in significant amounts as primary products. As each point on a product curve in Fig. 1 represents a separate analysis for that product, it is clear that the reproducibility is generally excellent. Minor amounts of butadiene are also observed, together with trace amounts of allene from some mixtures. In the later stages of reaction, propene oxide and isobutene oxide are detected as secondary products from propene and isobutene, respectively. Fig. 2 shows the effect of changing the diameter of the KCl-coated vessel from 5.2 to 1.8 cm. The rate of formation of all the products falls by a factor of ca. 2 except that of HDE which shows an increase. The general fall is consistent with a decrease in the chain length due to the surface destruction of HO_2 radicals. The increased rate of HDE formation is consistent with the mechanism, discussed later, in which for a given mixture composition a reduction in $[\text{HO}_2]$ gives increased [allyl] and HDE yields. Independent variation of the O_2 and DMP pressures has a relatively small effect on the product yields, which show little variation with temperature. Details of the effects of changes in mixture composition on the initial rates of formation of HDE and propene, can be seen in Table 5 (later).

Fig. 3 shows the product profiles for the mixture containing 4, 30 and 26 Torr of DMP, O_2 and N_2 , respectively, in an

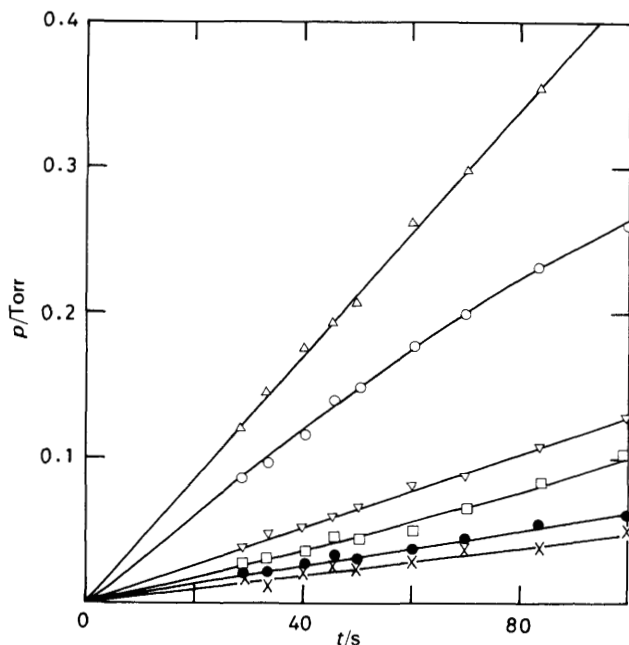


Fig. 2 Product yields in an 1.8 cm diameter KCl-coated vessel at 480 °C. DMP = 4, O₂ = 30, N₂ = 26 Torr. Δ, isobutene; ○, hexa-1,5-diene (×4); ▽, C₃H₆; □, CO; ●, acrolein; ×, C₂H₄

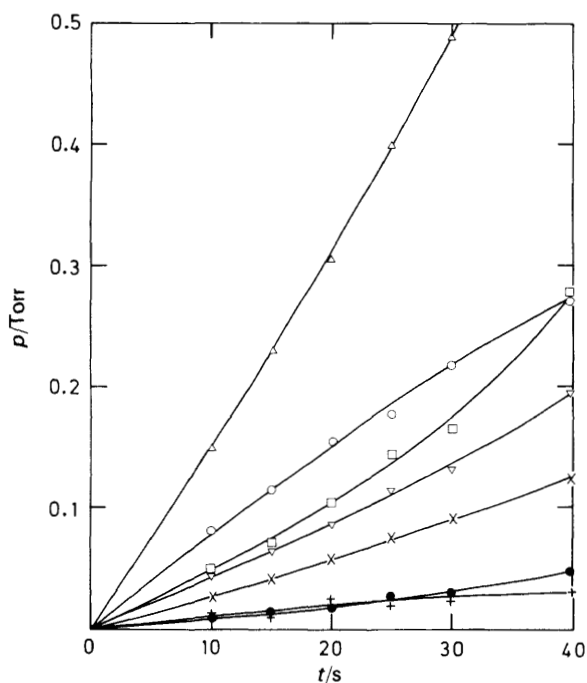


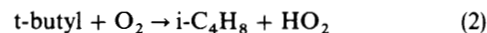
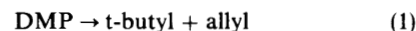
Fig. 3 Product yields in a 5.2 cm diameter aged boric-acid-coated vessel at 480 °C. DMP = 4, O₂ = 30, N₂ = 26 Torr. Δ, isobutene; ○, hexa-1,5-diene (×20); □, CO; ▽, C₃H₆; ●, acrolein; +, 4-methylpenta-1,3-diene

aged boric-acid-coated vessel at 480 °C, which in contrast to the KCl-coated vessel does not destroy peroxy radicals and H₂O₂ at the surface. Again very reproducible results are obtained and no new products are observed. The relative yields of most products are not greatly changed, but the relative yield of HDE is significantly lower and that of CO significantly greater than the yields observed in the KCl-coated vessel.

Attention in this paper is focused on the initial yields. Arising from the excellent reproducibility of the product yields and the essentially linear relationships with time, accurate values of the initial rates are obtained.

Discussion

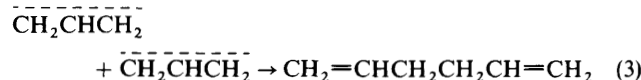
As suggested by Tsang's¹² work, and by the present product distribution, the basic mechanism of DMP decomposition in the presence of O₂ involves reactions (1) and (2).



As mentioned earlier, 99% of t-butyl radicals react with O₂ under the present conditions to give isobutene and HO₂,^{10,11} so that all other primary products are formed from allyl radicals or from radicals produced from DMP by H-atom abstraction. Formation of the primary products will be discussed in detail.

Hexa-1,5-diene (HDE)

The presence of HDE in relatively large yields (up to 15%) is a key observation, since the only plausible source is the recombination of allyl radicals.



In marked contrast, no trace of butane is observed under the same conditions in the oxidation of propionaldehyde which is an excellent source of C₂H₅ radicals.¹⁴ It must be concluded that allyl radicals are inert towards both O₂ and DMP, with the inescapable consequence that radical-radical processes of allyl become dominant. This feature is discussed later.

Isobutene

The sequence (1) and (2) is a major source of isobutene, and Tsang has suggested its formation in the molecular process (4).



If reactions (2) and (4) are the sole sources of isobutene, then the initial rate of formation of isobutene (R_i)₀ is given by equation (i)

$$(R_i)_0 = (k_4 + 0.99k_1)[\text{DMP}] \quad (i)$$

Table 2 shows that the values of (R_i)₀/[DMP] for a number of mixtures at 480 °C change systematically by a factor of ca. two in each vessel over a 20-fold range of DMP pressure. Two points emerge: (i) isobutene is not formed solely in the molecular process (4); and (ii) the small fall as DMP is reduced is almost certainly caused by a decreased contribution from isobutene formed as a result of a chain removal of DMP. Although the small effect may indicate a minor chain contribution to the removal of DMP, particularly at low DMP, radical attack on DMP by a reactive species such as OH will not change in importance as the pressure of DMP is decreased because in the initial stages of reaction OH radicals will react uniquely with DMP, in contrast to unreactive radicals such as HO₂ which will additionally undergo termination reactions.

Owing to the high C—H bond-dissociation energies in the —CH= and =CH₂ positions in DMP, H-atom abstraction will occur predominantly as shown in reactions (D) and (E).



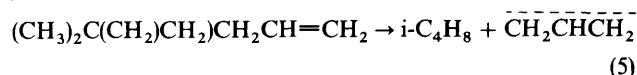
where X is mainly OH, HO₂ and CH₃. Radical R¹ will undergo rapid homolysis (5) to give isobutene and the allyl radical as the typical C—C bond-dissociation energy (ca. 135 kJ mol⁻¹) will be lowered by at least 50 kJ mol⁻¹ owing to

Table 2 Kinetic data at 480 °C^a

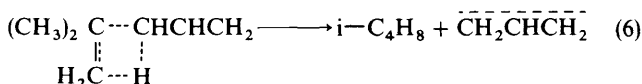
mixture composition/Torr			surface	10 ³ (R ₁) ₀ /[DMP]	10 ⁴ R _p /[DMP]	10 ² R _p R _{HDE} ^{1/2} [DMP]	10 ³ R _{CO} R _{HDE} ^{1/2} [O ₂]
DMP	O ₂	N ₂					
10	30	20	KCl	2.84	6.2	1.72	7.2
8	30	22	KCl	2.45	5.8	1.84	6.4
8	5	47	KCl	2.31	5.9	1.65	22.2
6	30	24	KCl	2.57	6.5	2.30	6.1
4	56	0	KCl	2.21	5.6	2.80	2.9
4	30	26	KCl	2.15	5.4	2.45	4.5
4	15	41	KCl	2.11	5.4	2.19	6.3
4	5	51	KCl	2.00	5.3	2.09	13.5
2	30	28	KCl	1.72	3.9	2.55	1.69
1	30	29	KCl	1.50	3.7	4.90	1.61
1	5	54	KCl	1.25	3.4	4.70	3.80
8	30	22	boric acid	4.9	11.2	4.40	20.4
4	30	26	boric acid	3.8	9.9	5.70	11.2
2	30	28	boric acid	3.2	8.0	8.0	8.2
0.5	30	29.5	boric acid	2.4	5.9	—	—

^a All quantities in Torr and s.

the delocalisation energy associated with the allyl radical and perhaps more arising from strain in radical R¹. Homolysis



of radical R² will also be favoured thermochemically, but will have a considerably higher activation energy than reaction (5) because of the strained four-centre transition state involved in the necessary H-atom transfer.



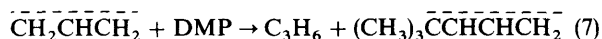
Propene

If initially propene is formed uniquely in reaction (4), then the rate of formation of propene is given by equation (ii)

$$R_p = (d[\text{C}_3\text{H}_6]/dt)_0 = k_4[\text{DMP}] \quad (\text{ii})$$

Table 2 shows that the values of R_p/[DMP] are not constant for different mixtures, but vary by a factor of *ca.* four. A further source of propene is thus required.

A metathesis reaction of allyl radicals with DMP will give propene, reaction (7) being the most energetically favourable possibility.



This possibility can be tested through application of eqn. (iii), which relates the initial rates of formation of propene and hexadiene. The values of (R_p/R_{HDE}^{1/2})/[DMP] are given in Table 2, and clearly vary considerably. It is concluded that reaction (7) is not a major source of propene.

$$(R_p/R_{\text{HDE}}^{1/2})/[\text{DMP}] = k_7/k_3^{1/2} \quad (\text{iii})$$

If propene is formed in both reactions (4) and (7), the rate of formation of propene is given by eqn. (iv), which on rearrangement gives eqn. (v).

$$R_p = k_4[\text{DMP}] + k_7 R_{\text{HDE}}^{1/2}[\text{DMP}]/k_3^{1/2} \quad (\text{iv})$$

$$R_p/[\text{DMP}] = k_4 + k_7 R_{\text{HDE}}^{1/2}/k_3^{1/2} \quad (\text{v})$$

Fig. 4 shows a plot of R_p/[DMP] vs. R_{HDE}^{1/2} at 480 °C. The correlation is poor, and in particular the results from the aged boric-acid-coated vessel are completely inconsistent with those from the KCl-coated vessel. At 400 and 440 °C, the correlation is even worse. From the line of lowest reason-

able gradient through the points from the KCl-coated vessel in Fig. 4, the value of k₇/k₃^{1/2} = 2.4 (dm³ mol⁻¹ s⁻¹)^{1/2} at 480 °C. Use of k₃ = 3.0 × 10⁹ (discussed later) gives k₇ = 1.3 × 10⁵ dm³ mol⁻¹ s⁻¹. Very little kinetic information is available on allyl radicals, but the value of k₇ is significantly higher than rate constants at 480 °C for alkyl + RH abstraction reactions of similar enthalpy change.¹⁵ Further, owing to the delocalisation effect, the value of A₇ may be a factor of up to 10 lower than A (alkyl + RH). It is unlikely that the maximum value of k₇ exceeds 1 × 10⁴ at 480 °C, compared with the minimum value of k₅ required from eqn. (v) and Fig. 4. It is concluded that reaction (7) is a negligible source of propene in the present study.

The formation of HDE in relatively large yields confirms the inertness of the allyl radical, and suggests that their reaction with other stable radicals may be important. Arising from reaction (2), HO₂ will be present in high concentration, so that reaction (8) would be both an important source of propene and a major termination process.

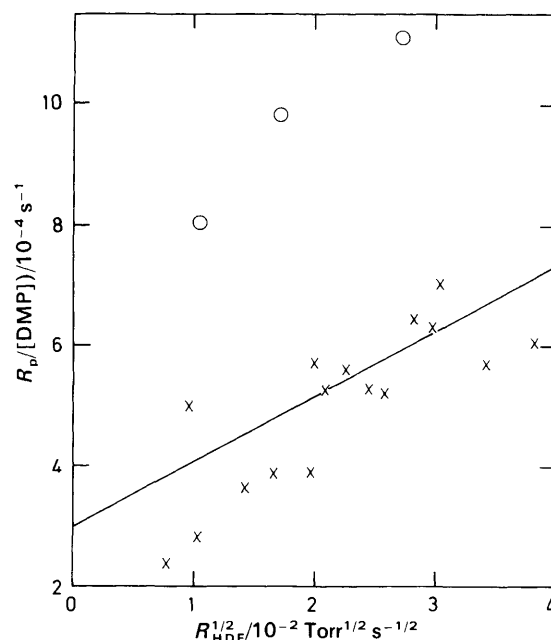
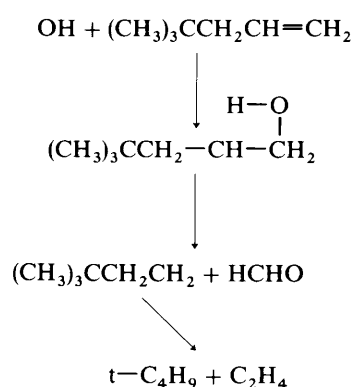


Fig. 4 R_p/[DMP] vs. R_{HDE}^{1/2} at 480 °C. ×, KCl-coated vessel; ○, aged boric-acid-coated vessel

As $[\text{HO}_2]$ will be higher in the aged boric-acid-coated vessel, the occurrence of reaction (8) would explain why the yields of propene are higher in this vessel than in the KCl-coated vessel. Reaction (8) will be discussed further in the section on CO formation.

Ethene

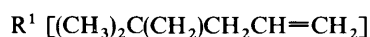
The values of the initial rate of formation of ethene divided by $[\text{DMP}]$ are relatively constant in KCl-coated vessels, which suggests a direct molecular formation from DMP. However, the ratio more than doubles in the boric-acid-coated vessel. The radical-radical reaction (9) cannot be eliminated, but it is difficult to suggest a reasonable mechanism. A more plausible route for ethene formation involves OH addition at the favoured terminal position in DMP.



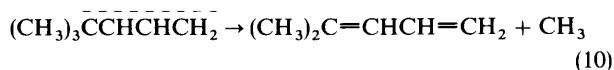
Formation of ethene in a disproportionation of two allyl radicals can be eliminated, because although butadiene is observed as a minor product, the ratio $[\text{C}_2/\text{H}_4]/[\text{butadiene}]$ is *ca.* 8.

4-Methylpenta-1,3-diene and Methane

Arising from its structure, the diene is almost certainly formed either from radical

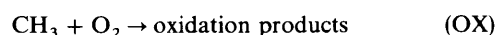


or from radical $\text{R}^2 [(\text{CH}_3)_3\text{CCHCHCH}_2]$, produced by radical attack on DMP. As indicated earlier R^1 has a facile homolysis (5) to give allyl and isobutene. Assuming that the bond-dissociation energies of the primary C-H bonds in DMP and ethane are the same, then ΔH_5 is only *ca.* 33 kJ mol⁻¹. However, the reverse addition of allyl to isobutene should have a high activation energy. Work by Nohara and Sakai¹⁶ suggests that $E_{-5} \approx 40$ kJ mol⁻¹, but the results are unreliable, and a value of 80–90 kJ mol⁻¹ is recommended, obtained from the addition of the delocalisation energy of the allyl radical to the mean value for the addition of ethyl and propyl radicals to double bonds.¹⁵ With $\Delta H_5 = 33$ kJ mol⁻¹, then $E_5 \approx 120$ kJ mol⁻¹. In combination with a minimum value of $A_5 = 10^{13.5}$ s⁻¹, then $k_5 \geq 1.5 \times 10^5$ s⁻¹ at 480 °C. At the low concentrations of O_2 used here ($< 6 \times 10^{-4}$ mol dm⁻³), with $k < 10^7$ dm³ mol⁻¹ s⁻¹ for reaction of radical R^1 with O_2 ⁵ (conjugate formation is not possible) then effectively homolysis is the sole reaction of R^1 . For the homolysis of radical R^1 into isobutene and allyl (6), $\Delta H_6 \approx 100$ kJ mol⁻¹, and with E_{-6} at least 80–90 kJ mol⁻¹ then $k_6/k_5 \approx 10^{-4}$ at 480 °C, so that $k_6 \approx 10$ s⁻¹. Consequently, R^2 radicals will undergo alternative reactions such as the homolysis (10) to give 4-methylpenta-1,3-diene and CH_3 .



Thermochemical calculations suggest that $A_{10} \approx 10^{14.5}$ s⁻¹ (an increased entropy of activation due to loss of electron delocalisation) and $E_{10} = 165$ kJ mol⁻¹, so that $k_{10} \approx 1.0 \times 10^3$ s⁻¹ at 480 °C. Unless a plausible alternative reaction with O_2 can be found with $k > 10^6$ dm³ mol⁻¹ s⁻¹, then (10) will be the predominant reaction of R^2 radicals under the present conditions. In confirmation of this conclusion, the yield of the diene is independent of $[\text{O}_2]$ over the range 5–30 Torr.

Methane will be formed through H-atom abstraction from DMP by CH_3 radicals, which will produce radicals R^1 and R^2 . As the yield of methane is relatively insensitive to the pressure of oxygen, then the CH_3 -abstraction processes must compete favourably with the oxidation of CH_3 radicals, expressed by the overall reaction (OX), as expected from previous studies¹⁷ which show that direct oxidation of CH_3 by molecular oxygen is slow.

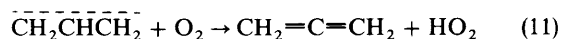


Allene (and Rate Constants for Alkenyl + O_2)

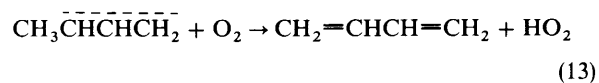
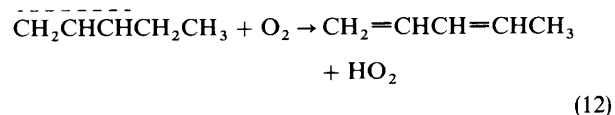
Traces of allene were observed in the products from a few mixtures. As the allene is likely to be formed in reaction (11), then the relative initial rates of formation of allene and HDE are related through eqn. (vi).

$$R_{\text{allene}}/R_{\text{HDE}}^{1/2}[\text{O}_2] = k_{11}/k_3^{1/2} \quad (\text{vi})$$

From the limited results available, $k_{11}/k_3^{1/2} = (4.3 \pm 1.5) \times 10^{-3}$ (dm³ mol⁻¹ s⁻¹)^{1/2} at 480 °C, so that with $k_3 = 3.0 \times 10^9$ then $k_{11} = (2.5 \pm 1) \times 10^2$ dm³ mol⁻¹ s⁻¹.



This value is considerably lower than the values of $10^{7.5}$ – $10^{8.5}$ dm³ mol⁻¹ s⁻¹ for the analogous reactions of alkyl radicals with O_2 to give the conjugate alkene and HO_2 .⁵ However, these reactions are markedly exothermic, $\Delta H = -40$ to -60 kJ mol⁻¹, whereas $\Delta H_{11} = +40$ kJ mol⁻¹. A marked variation of the value of k at 480 °C for this type of reaction with ΔH has been observed for other alkenyl radicals. Baldwin *et al.*¹⁸ give $k_{12} = 2.1 \times 10^6$, where $\Delta H_{12} = -21$ kJ mol⁻¹, and recent studies of the oxidation of (*E*)-but-2-ene give a value of k_{13} of *ca.* 2×10^5 dm³ mol⁻¹ s⁻¹ at 480 °C with $\Delta H = -6$ kJ mol⁻¹.



Baldwin *et al.*¹⁸ have given an Evans–Polanyi type of expression for the variation of rate constant at 480 °C with ΔH for this type of reaction of alkyl and alkenyl radicals with O_2 of the form, $\log[k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (per C-H bond)}] = A - B\Delta H$ over the range -14 to -60 kJ mol⁻¹ where A and B are constants. Fig. 5 shows a plot of $\log k$ vs. ΔH for all the available^{18,19} data at 480 °C. A satisfactory straight line may be drawn through the points, and eqn. (vii) gives a good representation of the data for ΔH between $+40$ and -60 kJ mol⁻¹.

$$\log[k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (per C-H bond)}] = 4.7 - 0.0525 \Delta H \quad (\text{vii})$$

Although a straight line may be drawn, the curve shown in Fig. 5 is probably more realistic, since the ratio (change in activation energy/change in ΔH) falls from virtually one for

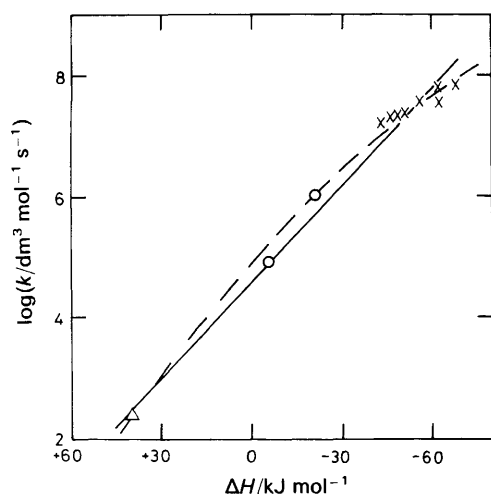
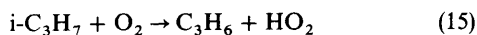
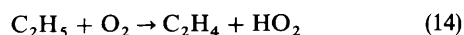


Fig. 5 $\log k$ at 480°C vs. ΔH for the reactions of alkyl and alkenyl radicals with O_2 . Dashed curve shows more realistic relationship. \times , Alkyl + O_2 ; \circ , alkenyl + O_2 ; Δ , allyl + O_2

very endothermic processes to almost zero for very exothermic processes.²⁰ As Gutman and co-workers²¹ have shown for reaction (14) and Walker and co-workers^{6,22} have shown for reactions (14) and (15), the activation energies of alkyl + O_2 reactions are zero or possibly slightly negative over the range 650–1000 K. Consequently over this temperature range, eqn. (vii) will give values of k (alkyl + $O_2 \rightarrow$ alkene + HO_2) accurate to a factor of *ca.* 2. Table 3 gives the activation energies for the three alkenyl + O_2 reactions discussed on the assumption that each has an A factor per C–H bond of $5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. No other kinetic information is available for these reactions.



Carbon Monoxide

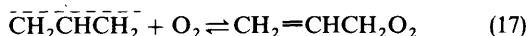
If CO is formed in the overall reaction



then the values of the initial rates of formation of CO and HDE are given by

$$R_{CO}/R_{HDE}^{1/2}[O_2] = k_{16}/k_3^{1/2} \quad (\text{viii})$$

As shown in Table 2, the values of $R_{CO}/R_{HDE}^{1/2}[O_2]$ vary considerably with mixture composition, which shows clearly that reaction (16) is not a major source of CO. This is consistent with the difficulty that allyl radicals have in reacting with O_2 owing to the unfavourable position of the equilibrium (17).



Pilling and co-workers²³ have measured the equilibrium constant of reaction (17) and give $\Delta H_{17} = -75 \text{ kJ mol}^{-1}$, compared with values of at least -120 kJ mol^{-1} for the

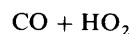
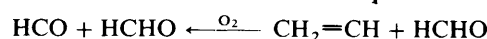
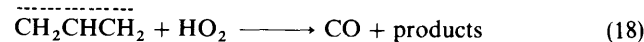
Table 3 Activation energies for 'stable' alkenyl + $O_2 \rightarrow$ diene + HO_2 reactions

reaction	$E/\text{kJ mol}^{-1}$
$\text{CH}_2\text{CHCHCH}_2\text{CH}_3 + O_2 \rightarrow \text{CH}_2=\text{CHCH}=\text{CHCH}_3 + HO_2$	24.2
$\text{CH}_3\text{CHCHCH}_2 + O_2 \rightarrow \text{CH}_2=\text{CHCH}=\text{CH}_2 + HO_2$	41.5
$\text{CH}_2\text{CHCH}_2 + O_2 \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + HO_2$	76.5

A (per C–H bond) assumed as $10^{7.70} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

alkyl + $O_2 \rightleftharpoons$ alkyl O_2 equilibria. In consequence the ceiling temperature (defined here as the temperature at which $[RO_2]/[R] = 1$ at $O_2 = 0.1 \text{ atm}$) occurs at *ca.* 280°C, *ca.* 200°C lower than for the alkyl–alkylperoxy systems. Consequently any oxidation of allyl through the allylperoxy species will be slow and normally of minor importance.

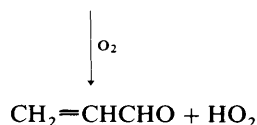
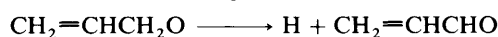
Given the relatively high yield of HDE and the high concentrations of HO_2 radicals, the most likely source of CO will be the overall radical–radical reaction (18), through the sequence shown.



Independent studies^{24,25} of the reaction of $\text{CH}_2=\text{CH}$ radicals with O_2 show that it is fast ($k > 10^9 \text{ mol}^{-1} \text{ s}^{-1}$ at 500°C) and that the products are uniquely HCHO and HCO, which then react further with O_2 to give solely HO_2 and CO.

Acrolein and Acetone

Loss of an H atom from the $\text{CH}_2=\text{CHCH}_2O$ radical, formed through the reaction of allyl and HO_2 , either by C–H homolysis or by reaction with O_2 would lead to the formation of acrolein. The initial value of $[\text{acrolein}]/[\text{CO}] \approx 0.15\text{--}0.20$ and is not sensitive to the pressure of O_2 , so that if CO and acrolein are both formed mainly from the $\text{CH}_2=\text{CHCH}_2O$ radical then reaction of this radical with O_2 must at most be of minor importance.



No obvious pathway for the formation of acetone is available. Formation from the allyl radical is unlikely because studies²⁶ of propene oxidation at 480°C, where allyl is a major propagating species, show copious yields of CO and acrolein but no acetone. Reactions of the radicals R^1 and R^2 provide a possible route. Although, as indicated earlier, R^1 undergoes a rapid homolysis to give isobutene and CH_2CHCH_2 , addition of O_2 followed by a concerted decomposition could lead to acetone.

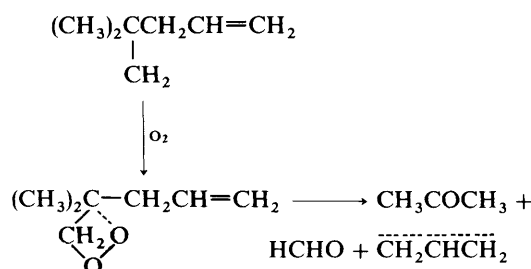
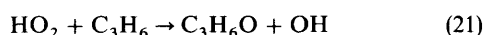


Table 5 Summary of results for the calculation of k_8 and k_{18} at 480 °C

mixture composition/Torr			$10^4 R_{\text{HDE}} / \text{Torr s}^{-1}$	$10^3 R_p / \text{Torr s}^{-1}$	$10^4 [\text{HO}_2] / \text{Torr}$	$10^4 [\text{allyl}] / \text{Torr}$	$10^{-9} k_8 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-9} k_{18} / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
DMP	O ₂	N ₂						
10	30	20	13.0	6.2	3.3	1.43	3.7	7.8
8	30	22	9.8	4.6	2.9	1.23	3.5	8.0
8	5	47	13.0	4.75	2.5	1.43	3.5	5.2
4	56	0	4.1	2.25	1.92	0.80	3.7	9.9
4	30	26	4.8	2.15	1.75	0.87	3.0	8.1
4	15	41	6.0	2.15	1.83	0.97	3.0	8.1
4	5	51	6.5	2.10	1.81	1.01	2.8	4.4

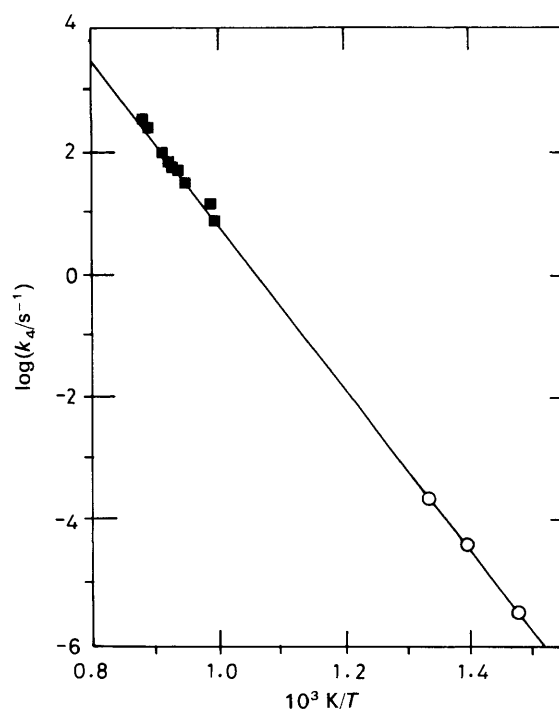
R_{HDE} and R_p can be measured directly, $k_4 = (2.5 \pm 0.5) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 480 °C from above, and $k_1 = (7.5 \pm 1.2) \times 10^{-4} \text{ s}^{-1}$ has been obtained²⁸ from studies of the addition of C₂H₆ to the DMP + O₂ system. As $R_{20} = 0.072 \text{ Torr}^{-1/2} \text{ s}^{-1/2}$ at 60 Torr at 480 °C has been obtained earlier²⁷ and $k_{19} = 1.87 \times 10^9 \exp(-775/T)$ then $[\text{HO}_2]$ may be calculated by use of eqn. (xv), and the values for each mixture used are given in Table 5 together with the values of $[\text{allyl}]$ which are calculated from the initial rates of formation of hexadiene ($R_{\text{HDE}} = k_3[\text{allyl}]^2$). A value of $k_3 = 3.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 400 and 500 °C is adopted here, based on an analysis of the available data given by Kerr and Moss.¹⁵ The values of k_8 and k_{18} obtained from the initial rates of formation of propene and CO are also given in Table 5 for each mixture. The variation for both rate constants is reasonable in view of the method of calculation, and mean values of $k_8 = (3.3 \pm 0.9) \times 10^9$ and $k_{18} = (7.4 \pm 2.4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 480 °C are recommended. No previous estimates of these rate constants are available in the literature.

A more reliable evaluation of $[\text{HO}_2]$ is clearly desirable and further studies are planned with C₃H₆ as additive to the DMP + O₂ system. As propene oxide is formed uniquely in reaction (21) and k_{21} is known²⁹ accurately, then $[\text{HO}_2]$ may be calculated from the initial rate of formation of propene oxide.

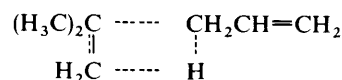


Arrhenius Parameters for Reaction (4)

The present values of k_4 (Table 4) over the range 400–480 °C have been combined with values calculated from the shock-tube results obtained between 1000 and 1300 K by Tsang,¹² who observed propene as an initial product in the decomposition of DMP. On the basis that the propene found by Tsang was formed only in reaction (4), then the values of k_4 from his results are shown in Arrhenius form in Fig. 7, together with the present values. From the excellent line through the two sets of data, linear regression gives $\log(A_4/\text{s}^{-1}) = 14.19 \pm 0.25$ and $E_4 = 255.5 \pm 5.3 \text{ kJ mol}^{-1}$.

**Fig. 7** Arrhenius plot for reaction (4). ■, Tsang;¹² ○, present work

These parameters appear to be the first reported for the molecular decomposition of an alkene, but as shown in Table 6 they are very similar to those for related molecular decompositions of alkanes and ethers. Following Choo *et al.*'s suggestion that the decomposition of *t*-butyl methyl ether into *i*-C₄H₈ and CH₃OH occurs through a four-centre transition state, it is probable that the activated complex for reaction (4) may be represented as

**Table 6** Arrhenius parameters for the molecular decomposition of ethers and related compounds

reactant	products	$T/^\circ\text{C}$	$\log(A/\text{s}^{-1})$	$E/\text{kJ mol}^{-1}$	ref.
<i>t</i> -butyl methyl ether	<i>i</i> -C ₄ H ₈ + MeOH	615–850	13.9	246.9	30
		433–495	14.4	257.9	^a
<i>t</i> -butyl ethyl ether	<i>i</i> -C ₄ H ₈ + EtOH	433–484	14.1	249.8	^b
<i>t</i> -butyl isopropyl ether	<i>i</i> -C ₄ H ₈ + Pr ⁱ OH	409–475	13.4	232.2	^c
		C ₃ H ₆ + Bu ⁱ OH	409–475	13.0	236.3
2,2,3,3-tetramethylbutane	<i>i</i> -C ₄ H ₈ + isobutane	420–540	13.89	275.0	31
diisopropyl ether	C ₃ H ₆ + Pr ⁱ OH	423–487	14.6	265.7	^d
4,4-dimethylpent-1-ene	<i>i</i> -C ₄ H ₈ + propene	400–857	14.2	255.0	present work

^a N. J. Daly and C. Wentrup, *Aust. J. Chem.*, 1970, **23**, 541. ^b N. J. Daly and C. Wentrup, *Aust. J. Chem.*, 1968, **21**, 1535. ^c N. J. Daly and C. Wentrup, *Aust. J. Chem.*, 1970, **23**, 541. ^d N. J. Daly and V. R. Stimson, *Aust. J. Chem.*, 1966, **19**, 239.

A simple theoretical estimate of A_4 based on transition-state theory may be made by use of the equation $A = (ek_B T/h)\exp(\Delta S^\ddagger/R)$ where ΔS^\ddagger is the entropy of activation. The calculation of $\Delta S_4^\ddagger = 4.0 \text{ J K}^{-1} \text{ mol}^{-1}$ is similar to that carried out for the molecular decomposition of tetramethylbutane into isobutane and isobutene.³¹ At 1000 K, the mean temperature of the results in Fig. 7, use of the transition-state equation gives $A_4 = 10^{14.0} \text{ s}^{-1}$, in excellent agreement with the experimental value.

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