# Oxidation of Allyl Radicals: Kinetic Parameters for the Reactions of Allyl Radicals with HO$_2$ and O$_2$ between 400 and 480 °C
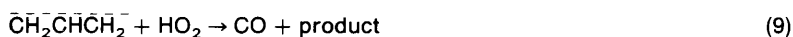
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The decomposition of 4,4-dimethylpent-1-ene (DMP) in the presence of O$_2$ has been used as a source of allyl and HO$_2$ radicals between 400 and 480 °C. Propene was added to the mixtures of DMP and O$_2$ in order to monitor [HO$_2$] from the yields of propene oxide by use of the known value of $k_{14}$.

$$HO_2 + C_3H_6 \rightarrow C_3H_6O + OH \tag{14}$$
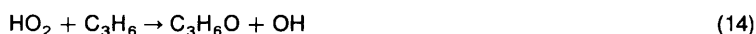
From measurements of the initial yields of CO, hexa-1,5-diene and propene oxide over a range of mixture composition, rate constants have been obtained for reactions (9) and (10).

$$\overline{CH_2CHCH_2}^- + HO_2 \rightarrow CO + \text{product} \tag{9}$$

$$\overline{CH_2CHCH_2}^- + HO_2 \rightarrow C_3H_6 + HO_2 \tag{10}$$

At 400 °C, $k_9 = 3.95 \times 10^9$ and $k_{10} = 1.42 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and both show a slight increase (within experimental error) with temperature, 15% and 30%, respectively, at 480 °C.

Strong evidence is obtained for the formation of CO in the reaction between allyl radicals and O$_2$ [reaction (15)] and values of $A_{15} = 10^{9.4 \pm 0.6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_{15} = 79 \pm 8$ kJ mol$^{-1}$ are obtained.

$$\overline{CH_2CHCH_2}^- + O_2 \rightarrow CO + \text{products} \tag{15}$$

The mechanisms of reactions (10) and (15) are discussed. Based on current thermochemistry it is shown by calculation that reaction (10) probably occurs only to a minor extent through a direct H-atom abstraction route which is the reverse of the chain initiation reaction (16).

$$C_3H_6 + O_2 \rightarrow \overline{CH_2CHCH_2}^- + HO_2 \tag{16}$$

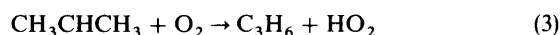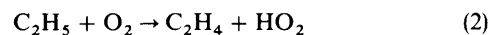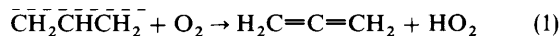The available kinetic data for the reaction between allyl radicals and O$_2$ are summarised.

As indicated earlier,[1,2] very little is known about the oxidation chemistry of allyl and allyl-related radicals, despite their key role in both combustion and atmospheric chemistry. Their importance and interest arise from both their ease of formation and their coupled inertness[1,2] towards reaction with oxygen, hydrocarbons or indeed any organic molecular species. The radicals are readily formed because the energy barrier to the abstraction of H atoms in a position $\beta$ to a double bond in alkenes is lowered through electron delocalisation in the emerging radical. As the activation energy for H-atom abstraction by OH radicals from the $\beta$ position in alkenes will be zero, formation of electron-delocalised radicals will occur even under atmospheric conditions.

Stable, electron-delocalised radicals also play a major role in the combustion of alkylbenzenes, for example, benzyl from toluene, PhCHCH$_3$ from ethylbenzene, and Ph(CH$_3$)CH$_2$ from the xylenes. Between 350 and 1000 °C, H-atom abstraction is the main process for attack on the alkylbenzenes,[3] and in consequence reactions of the delocalised radicals are important propagation and termination steps in the oxidation.

Within a few kJ mol$^{-1}$, the delocalised radicals are all effectively thermally stabilised[4] by *ca.* 60 kJ mol$^{-1}$, so that reactions with O$_2$ and hydrocarbons are much slower than the analogous reactions of alkyl radicals. This is convincingly demonstrated in the case of allyl radicals by the formation of hexa-1,5-diene (from the recombination of allyl radicals) in yields of *ca.* 20% from a mixture containing 4, 30 and 26 Torr† of propene, oxygen and nitrogen, respectively, at 500 °C.[5]

The following three points elucidate the lack of reactivity in the allyl radical, and all arise from the stabilisation energy

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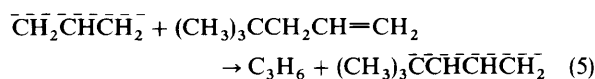
† 1 Torr = 101 325/760 Pa.

caused by delocalisation. (i) Whereas 99% of ethyl radicals and 95% of 2-propyl radicals react with oxygen under combustion conditions between 350 and 750 °C to give the conjugate alkene and HO$_2$, only traces of allene are observed from allyl radicals under similar conditions.[2] A preliminary value of $k_1 = (2.5 \pm 1) \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 480 °C has been obtained[2] from studies of the decomposition of 4,4-dimethylpent-1-ene in the presence of O$_2$, compared with well established[6,7] values of $k_2 = 3.0 \times 10^7$ and $k_3 = 1.2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, consistent with the large differences in $\Delta H_1 = +40$, $\Delta H_2 = -50$ and $\Delta H_3 = -58$ kJ mol$^{-1}$ at 480 °C.

$$\overline{CH_2CHCH_2}^- + O_2 \rightarrow H_2C=C=CH_2 + HO_2 \tag{1}$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \tag{2}$$

$$CH_3CHCH_3 + O_2 \rightarrow C_3H_6 + HO_2 \tag{3}$$

(ii) Oxidation through allylperoxy radicals will be unimportant (unlike the major routes observed[8] for alkylperoxy radicals) because of the unfavourable position of the equilibrium in reaction (4), with $\Delta H_4 = -75$ kJ mol$^{-1}$ compared with enthalpy changes of at least $-130$ kJ mol$^{-1}$ for the formation of ethylperoxy and 2-propylperoxy radicals.[9]

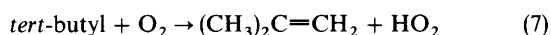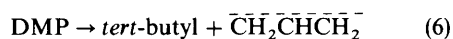$$\overline{CH_2CHCH_2}^- + O_2 \rightarrow H_2C=CHCHO_2 \tag{4}$$
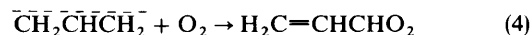
(iii) H-atom abstraction by allyl radicals from alkanes will have a high activation energy (70–130 kJ mol$^{-1}$). Recent studies[2] have shown that negligible amounts of propene are formed even in the energetically favourable reaction (5) under conditions similar to those outlined above.
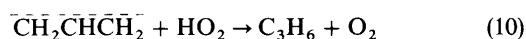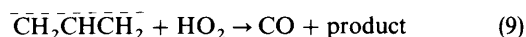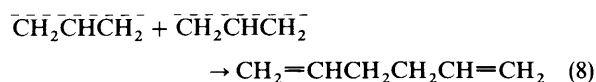
$$\overline{CH_2CHCH_2}^- + (CH_3)_3CCH_2CH=CH_2$$
$$\rightarrow C_3H_6 + (CH_3)_3\overline{CCHCHCH_2}^- \tag{5}$$

Arising from their thermal stability, it is not surprising that allyl radicals react mainly through radical–radical processes

under combustion conditions. Lodhi and Walker[2] have shown that the decomposition of 4,4-dimethylpent-1-ene (DMP) in the presence of $O_2$ provides an excellent source of $HO_2$ and allyl radicals between 400 and 500 °C, as indicated by the basic mechanism, reactions (6) and (7).

$$DMP \rightarrow tert\text{-butyl} + \overline{CH_2CHCH_2} \qquad (6)$$

$$tert\text{-butyl} + O_2 \rightarrow (CH_3)_2C{=}CH_2 + HO_2 \qquad (7)$$

The major reactions of allyl radicals are then reactions (8)–(10).

$$\overline{CH_2CHCH_2} + \overline{CH_2CHCH_2}$$
$$\rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 \quad (8)$$

$$\overline{CH_2CHCH_2} + HO_2 \rightarrow CO + product \qquad (9)$$

$$\overline{CH_2CHCH_2} + HO_2 \rightarrow C_3H_6 + O_2 \qquad (10)$$

Based on the assumption that CO is formed uniquely in reaction (9), and propene in reactions (10) and (11), Lodhi and Walker[2] were able to obtain values of $k_{11}$ and $k_{10}/k_9$ by use of eqn. (i), where $R_P$ and $R_{CO}$ are the initial rates of formation of propene and CO, respectively.

$$DMP \rightarrow (CH_3)_2C{=}CH_2 + C_3H_6 \qquad (11)$$
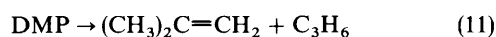
$$R_P/[DMP] = k_{11} + R_{CO}k_{10}/k_9[DMP] \qquad (i)$$

By equating the rate of initiation [reaction (6)] to the total rate of termination through reactions (8), (10), (12) and (13), approximate values of the $HO_2$ concentration were calculated for a series of mixtures.[2] In combination with eqn. (ii), below, for the initial rate of formation of hexadiene, preliminary values of $k_9 = (7.4 \pm 2.4) \times 10^9$ and $k_{10} = (3.3 \pm 0.9) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 480 °C were obtained.[2]

$$R_{HDE} = k_8[\overline{CH_2CHCH_2}]^2 \qquad (ii)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (12)$$

$$HO_2 \rightarrow surface \qquad (13)$$
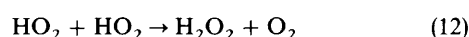
In the present study, $C_3H_6$ has been added to DMP–$O_2$ mixtures, and $[HO_2]$ monitored [eqn. (iii)] from the initial rates of formation of propene oxide ($R_{PO}$) which is formed in

reaction (14). The value of $k_{14}$ is known accurately from studies[10] of the decomposition of tetramethylbutane in the presence of $O_2$ (which provides an excellent source of $HO_2$) and propene over the range 380–520 °C.

$$HO_2 + C_3H_6 \rightarrow C_3H_6O + OH \qquad (14)$$
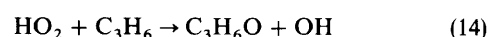
$$[HO_2] = R_{PO}/k_{14}[C_3H_6] \qquad (iii)$$

## Experimental

Details of the experimental procedure have been given earlier.[2]

Both KCl-coated (fresh each week) and aged boric-acid-coated cylindrical Pyrex vessels were used in this study. Precise admission and sampling times were achieved by use of solenoid valves which had a response time of less than 0.1 s. Quantitative product analysis was carried out by gas chromatography. For the kinetic measurements, the consumption of DMP and $C_3H_6$ never exceeded 3%.

## Results and Discussion

Studies were made at a total pressure of 60 Torr and at temperatures of 400, 440 and 480 °C with emphasis on initial-product yields. The aged boric-acid-coated vessel was used at all three temperatures and the KCl-coated vessel was also used at 480 °C. Several mixtures were studied at each temperature (see Table 1). Fig. 1 shows [product]–time profiles for the boric-acid-coated vessel for the mixture containing 4, 4, 30 and 22 Torr of DMP, propene, $O_2$ and $N_2$, respectively. Acetaldehyde is the only new product observed when propene is present,[2] but the yield of propene oxide is significantly increased as expected. Plots of similar precision were obtained for all mixtures under all conditions used. For all mixtures in both types of vessel at each temperature used, the major products were isobutene, propene oxide, CO, ethene and hexa-1,5-diene (HDE). The quality of the data is consistently good, so that reliable initial rates may be obtained by computer fitting. Here the important parameters are $R_{PO}$,

**Table 1** Initial rates of formation of CO, HDE and propene oxide

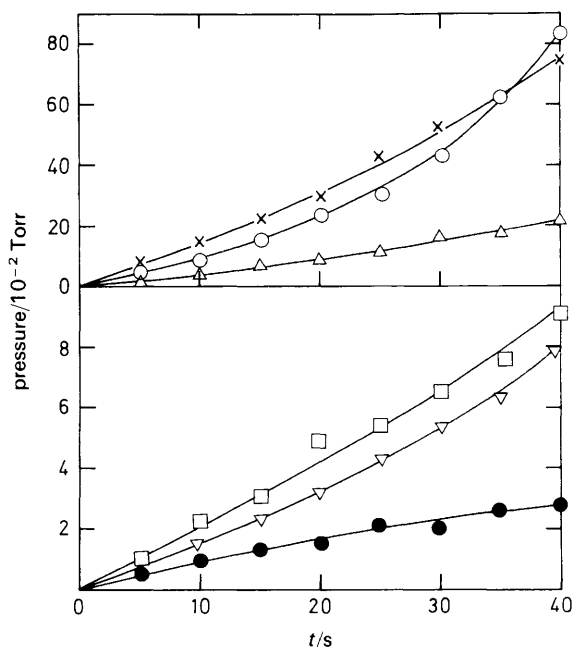| partial pressure of mixture components/Torr | | | | rate/$10^{-4}$ Torr s$^{-1}$ | | | $\dfrac{R_{CO}[C_3H_6]}{R_{HDE}^{1/2}R_{PO}}\bigg/ \text{Torr}^{1/2}\,\text{s}^{1/2}$ |
|---|---|---|---|---|---|---|---|
| DMP | $C_3H_6$ | $O_2$ | $N_2$ | $R_{HDE}$ | $R_{CO}$ | $R_{PO}$ | |
| aged boric-acid-coated vessels, 480 °C | | | | | | | |
| 4 | 4 | 30 | 22 | 9.1 | 84 | 22.7 | 490 |
| 1 | 10 | 30 | 19 | 9.3 | 24.0 | 13.8 | 570 |
| 1 | 3 | 30 | 26 | 3.2 | 20.5 | 6.5 | 529 |
| 1 | 3 | 5 | 51 | 4.5 | 14.0 | 4.5 | 440 |
| KCl-coated vessels, 480 °C | | | | | | | |
| 4 | 4 | 30 | 22 | 10.5 | 45 | 10.5 | 529 |
| 1 | 10 | 30 | 19 | 6.5 | 13.5 | 8.9 | 595 |
| 1 | 3 | 30 | 26 | 3.6 | 12.0 | 4.0 | 474 |
| 1 | 3 | 5 | 51 | 5.1 | 8.0 | 2.7 | 395 |
| aged boric-acid-coated vessels, 440 °C | | | | | | | |
| 4 | 4 | 30 | 22 | 1.08 | 6.8 | 3.2 | 818 |
| 4 | 4 | 5 | 47 | 0.78 | 2.25 | 1.37 | 743 |
| 1 | 10 | 30 | 19 | 0.68 | 1.54 | 1.06 | 1700 |
| 1 | 3 | 30 | 26 | 0.44 | 2.49 | 1.11 | 1015 |
| 1 | 3 | 5 | 51 | 0.40 | 0.91 | 0.58 | 744 |
| aged boric-acid-coated vessels, 400 °C | | | | | | | |
| 4 | 4 | 30 | 22 | 0.182 | 1.01 | 0.71 | 1350 |
| 4 | 4 | 5 | 47 | 0.093 | 0.221 | 0.228 | 1265 |
| 1 | 10 | 30 | 19 | 0.134 | 0.294 | 0.257 | 3120 |
| 1 | 3 | 30 | 26 | 0.065 | 0.37 | 0.192 | 2270 |
| 1 | 3 | 5 | 51 | 0.036 | 0.085 | 0.097 | 1370 |

**Fig. 1** Product yields in a 5.2 cm diameter aged boric-acid-coated vessel at 480 °C. Partial pressures/Torr: DMP = 4, $C_3H_6$ = 4, $O_2$ = 30, $N_2$ = 22. ×, isobutene; ○, CO; △, $C_2H_4$; □, propene oxide; ▽, $CH_3CHO$; ●, HDE

$R_{HDE}$ and $R_{CO}$, the initial rates of formation of propene oxide, HDE and CO, respectively, and the values are given in Table 1 for the conditions used. The other products from the decomposition of DMP have been discussed earlier.[2]

Based on initial products and assumed unique formation of CO in reaction (9), $R_{CO}$ is given by eqn. (iv).

$$R_{CO} = k_9[HO_2][\overline{C}\overline{H}_2\overline{C}\overline{H}\overline{C}\overline{H}_2] \qquad (iv)$$

Measurement of $R_{HDE}$ and $R_{PO}$, together with the use of eqn. (ii) and (iii), permits substitution for $[HO_2]$ and $[\overline{C}\overline{H}_2\overline{C}\overline{H}\overline{C}\overline{H}_2]$ into eqn. (iv) to give, on rearrangement, eqn. (v).

$$R_{CO}[C_3H_6]/R_{PO} R_{HDE}^{1/2} = k_9/k_{14} k_8^{1/2} \qquad (v)$$

The values of $R_{CO}[C_3H_6]/R_{PO} R_{HDE}^{1/2}$ are given in Table 1 for all conditions studied. At 480 °C, the values are nearly constant in both types of vessel, ranging between 595 and 395 $Torr^{1/2}$ $s^{1/2}$, which provides strong evidence that reaction (9) is the major source of CO. At 440 and 400 °C, the variation is slightly larger. As previous studies have established that reaction (14) provides a unique source of propene oxide under the present conditions,[10] and that HDE is formed solely in reaction (8),[2,5] then the most likely explanation of the variation shown in Table 1 is that CO is formed mainly in reaction (9) but also in an additional reaction.

Evidence for a further source of CO was found when the DMP–$O_2$ studies were modelled by computer treatment. If CO and HDE are formed uniquely in reactions (9) and (8), respectively, then $R_{CO}/R_{HDE} = k_9[HO_2]/k_8[\overline{C}\overline{H}_2\overline{C}\overline{H}\overline{C}\overline{H}_2]$.

All reasonable mechanisms tested with CO uniquely formed in reaction (9) suggest that $[HO_2]/[\overline{C}\overline{H}_2\overline{C}\overline{H}\overline{C}\overline{H}_2]$, and therefore $R_{CO}/R_{HDE}$, is effectively independent of $[O_2]$. However, the value of $R_{CO}/R_{HDE}$ increases steadily with $[O_2]$ and changes[1] by a factor of just over 2 between 5 and 56 Torr of $O_2$, which implies a further source of CO which becomes more important at high $[O_2]$. Reaction (15) is the most likely possibility.

$$\overline{C}\overline{H}_2\overline{C}\overline{H}\overline{C}\overline{H}_2 + O_2 \rightarrow CO + products \qquad (15)$$

With CO now produced in reactions (9) and (15), the values of $R_{CO}$, $R_{HDE}$ and $R_{PO}$ are related by eqn. (vi).

$$\frac{R_{CO}}{[O_2]R_{HDE}^{1/2}} = \frac{k_9 R_{PO}}{k_{14} k_8^{1/2}[C_3H_6][O_2]} + \frac{k_{15}}{k_8^{1/2}} \qquad (vi)$$

Plots of $R_{CO}/[O_2]R_{HDE}^{1/2}$ against $R_{PO}/[C_3H_6][O_2]$ are shown in Fig. 2 for all mixtures studied at 400, 440 and 480 °C. Good straight lines are obtained for all three temperatures and, based on eqn. (vi), values of $k_9/k_{14} k_8^{1/2}$ and $k_{15}/k_8^{1/2}$ are obtained from the gradients and intercepts, respectively. The values are summarised in Table 2. Use of the recommended[2] value of $k_8 = 3.0 \times 10^9$ $dm^3$ $mol^{-1}$ $s^{-1}$ between 400 and 500 °C, together with $k_{14} = 10^{9.01} \exp(-7530/T)$ $dm^3$ $mol^{-1}$ $s^{-1}$, obtained from independent studies[11,12] of the decomposition of tetramethylbutane in the presence of $O_2$ and
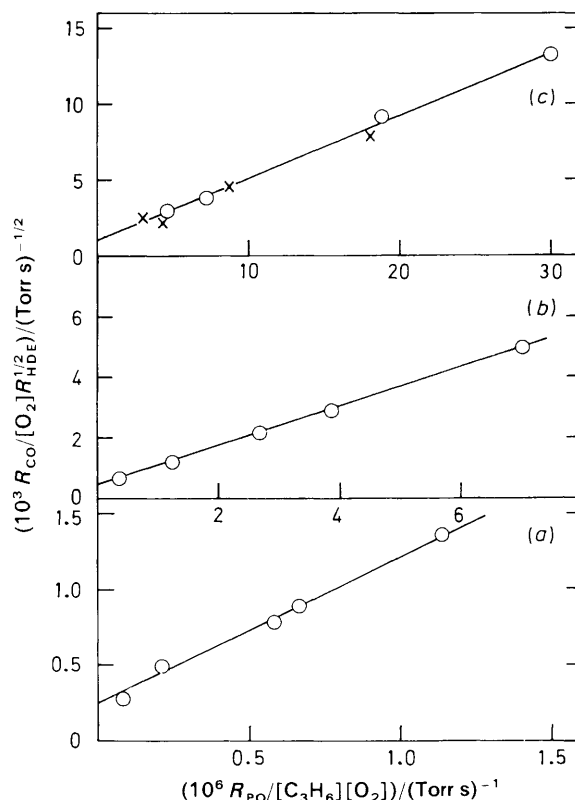


**Fig. 2** Plots of $R_{CO}/[O_2] R_{HDE}^{1/2}$ against $R_{PO}/[C_3H_6][O_2]$. ×, KCl-coated vessel; ○, aged boric-acid-coated vessel. (a) 400 °C; (b) 440 °C; (c) 480 °C
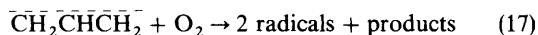
**Table 2** Summary of kinetic data

| $T/°C$ | $(k_9/k_{14} k_8^{1/2})/(mol\ dm^{-3}\ s^{-1})^{1/2}$ | $(k_{15}/k_8^{1/2})/(dm^3\ mol^{-1}\ s^{-1})^{1/2}$ | $k_9/dm^3\ mol^{-1}\ s^{-1}$ | $k_{10}/dm^3\ mol^{-1}\ s^{-1}$ | $k_{15}/dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|
| 400 | $4.95 \pm 0.55$ | $0.051 \pm 0.015$ | $3.85 \times 10^9$ | $1.42 \times 10^9$ | $2.8 \times 10^3$ |
| 440 | $2.94 \pm 0.21$ | $0.095 \pm 0.020$ | $4.3 \times 10^9$ | $1.63 \times 10^9$ | $5.2 \times 10^3$ |
| 480 | $1.74 \pm 0.19$ | $0.215 \pm 0.03$ | $4.45 \times 10^9$ | $1.87 \times 10^9$ | $1.18 \times 10^4$ |

propene, gives the absolute values of $k_9$ and $k_{15}$ summarised in Table 2. The value of $k_9$ at 480 °C is in reasonable agreement with the value of $(7.4 \pm 2.5) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ obtained from the DMP + O$_2$ studies[2] through an estimation of [HO$_2$], as outlined earlier.

The values of $k_9$ vary by less than 15% between 400 and 480 °C, which is within experimental error, so that effectively $k_9$ is independent of temperature as expected for a rate constant of the observed magnitude at ca. 500 °C. No independent values of $k_9$ are available in the literature. As indicated earlier, by use of eqn. (i) in the DMP + O$_2$ studies, Lodhi and Walker[2] obtained values of $k_{10}/k_9$ of $0.37 \pm 0.04$, $0.38 \pm 0.03$ and $0.42 \pm 0.04$ at 400, 440 and 480 °C. In combination with the present values of $k_9$, values of $k_{10}$ can be calculated and they are summarised in Table 2. A small positive increase with temperature is observed, but the variation is probably within experimental error.

The values of $k_{15}$ vary markedly with temperature and give Arrhenius parameters of $A_{15} = 10^{9.4 \pm 0.6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_{15} = 79 \pm 8$ kJ mol$^{-1}$. At 480 °C, the value of $k_{15}$ is a factor of ca. $10^4$ lower than typical rate constants for the reactions of alkyl radicals with O$_2$ to give conjugate alkene and HO$_2$ radicals, such as $k_2 = 3.0 \times 10^7$ and $k_3 = 1.2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, given earlier.

No independent value of $k_{15}$ is available, but in obtaining the Arrhenius parameters for the initiation reaction (16) from studies of the yields of hexadiene in the slow oxidation of propene between 400 and 520 °C by equating the rates of initiation and termination, Stothard and Walker[13] obtained strong kinetic evidence for the branching reaction (17) between allyl radicals and O$_2$, and obtained[13] $A_{17} = 10^{8.21 \pm 0.60}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_{17} = 72.5 \pm 8.3$ kJ mol$^{-1}$.

$$CH_3CH=CH_2 + O_2 \rightarrow \overline{CH_2CHCH_2^-} + HO_2 \qquad (16)$$

$$\overline{CH_2CHCH_2^-} + O_2 \rightarrow 2 \text{ radicals} + \text{products} \qquad (17)$$

They showed that these parameters are consistent with the formation of a cyclic intermediate from the CH$_2$=CHCH$_2$O$_2$ radical, as shown in path A in Scheme 1 below.
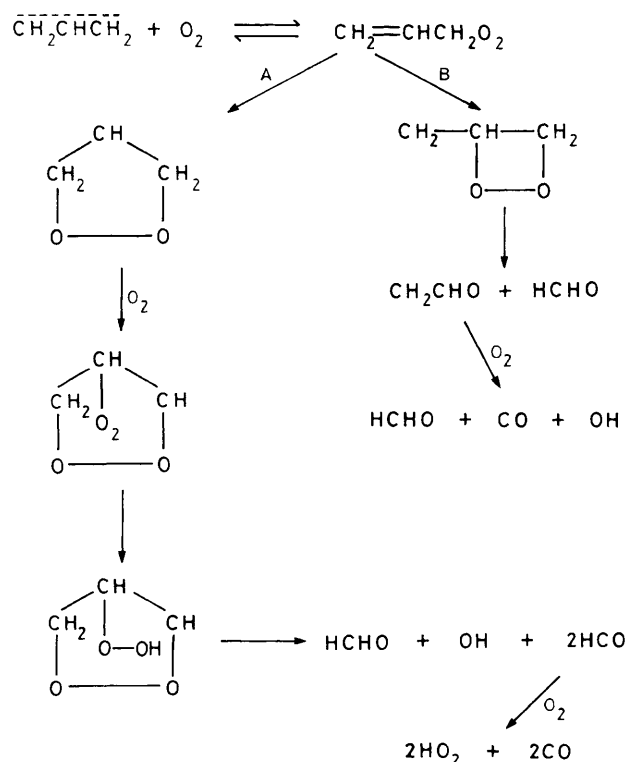
The relative rates of paths A and B are basically determined by the two parameters in the Arrhenius equation. First, the ratio of A factors, $A_B/A_A \approx 9$, owing to the extra loss of entropy of activation of ca. 18 J K$^{-1}$ mol$^{-1}$ in forming the five-membered ring in path A.[8] Secondly, however, the greater strain in the smaller ring (ca. 14 kJ mol$^{-1}$)[8] implies that A is the faster route by a factor of ca. 10 at ca. 480 °C, so that paths A and B should have similar rates.

From the present studies, the value of $k_{15}$ (= $1.18 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 480 °C) has been obtained from the total rate of CO formation in the reaction between allyl radicals and O$_2$. Application of Scheme 1 with the reaction $\overline{CH_2CHCH_2^-} + O_2 \rightleftharpoons CH_2=CHCH_2O_2$ equilibrated[1] (equilibrium constant $K$) then gives $k_{17} = Kk_A$ and eqn. (vii) for $k_{15}$.
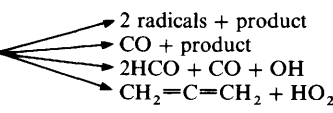
$$k_{15} = 2Kk_A + Kk_B \qquad (vii)$$

From the value of $k_{15}$, and $k_{17} = 1.6 \times 10^3$ mol$^{-1}$ s$^{-1}$ at 480 °C from the propene oxidation studies,[13] $Kk_B = 8.6 \times 10^3$, and the relative rate of paths A and B $(k_B/k_A)$ is ca. 2.7. This value is sufficiently close to the 'theoretically' derived value of ca. unity, bearing in mind the approximations made, that some support can be claimed for the proposed mechanisms in Scheme 1. Further conjecture is not justified because the values of $k_{15}$ (obtained from the intercept in Fig. 2) are not sufficiently accurate. Attempts are being made to find an allyl radical system where [HO$_2$] is much lower so that reaction (15) is the major source of CO with consequent increase in the reliability of the value of $k_{15}$ obtained. The available kinetic data for the different pathways involved in the reaction between allyl radicals and O$_2$ are summarised in Table 3.

A possible mechanism for reaction (9) has been discussed elsewhere.[2] Reaction (10) is most likely to proceed either through a direct abstraction route [the reverse of the initiation reaction (16)] or via a disproportionation transition state, which probably involves a six-membered ring.





Scheme 1
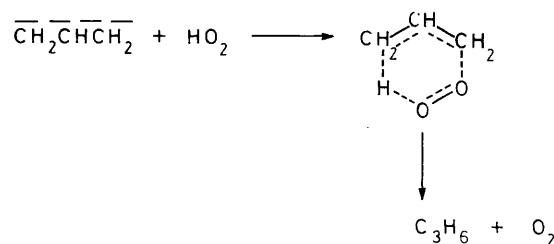
The value of $k_{16}$ has been determined accurately over the temperature range 400–520 °C,[13] so that the rate constant for the reverse process $k_{-16}$ can be estimated by use of thermochemical data. Recent upward revision of the enthalpies of formation of alkyl radicals[14] has cast some doubt on long accepted values for other radicals such as allyl. Values of $\Delta H_{f, 298}$ (allyl) of 164, 165, 170 and 172 kJ mol$^{-1}$ have been obtained or recommended,[4,15-17] and a value of $168 \pm 4$ kJ mol$^{-1}$ is adopted here, together with a consensus value for $S^0_{298}$ (allyl) of $260 \pm 2$ J K$^{-1}$ mol$^{-1}$. $\Delta H_{f, 298}$ (HO$_2$) is taken[18] as $(14 \pm 4)$ kJ mol$^{-1}$ and $S^0_{298}$ (HO$_2$) as 227.6 J K$^{-1}$ mol$^{-1}$. With the standard thermochemical values for propene and O$_2$, and $\Delta C_p$ effectively zero at ca. 250 °C, then at 480 °C $\Delta H_{16} = +161.5$ kJ mol$^{-1}$ and $\Delta S_{16} = +15.7$ J K$^{-1}$ mol$^{-1}$ so that the calculated value of $K_{16} = 4.2 \times 10^{-11}$. From their direct studies of $k_{16}$, Stothard and Walker[13] obtained $k_{16} = (8.9 \pm 1.5) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 480 °C, so that $k_{-16} = 2.1 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ compared with the present value of $k_{10} = 1.42 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. The direct abstraction route for C$_3$H$_6$ formation in the reaction between allyl and HO$_2$ radicals thus appears to play a minor role on the basis

**Table 3** Kinetic data for allyl + $O_2$ reaction pathways[a]

| pathway | $\log(A/dm^3\ mol^{-1}\ s^{-1})$ | $E/kJ\ mol^{-1}$ | ref. |
|---|---|---|---|
| $\dot{C}H_2CHCH_2 + O_2$ → 2 radicals + product | $8.2 \pm 0.6$ | $72.5 \pm 8.3$ | 13 |
| → CO + product | $9.0 \pm 0.6$ | $79 \pm 8$ | present |
| → 2HCO + CO + OH | $k = (8.6 \pm 2.3) \times 10^3$ (480 °C) | | present |
| → $CH_2$=C=$CH_2$ + $HO_2$ | $k = (2.5 \pm 1) \times 10^2$ (480 °C) | | 2 |

[a] Note that the four reactions are not independent (see text).

of current views of the thermochemistry. The value of $\Delta S_{16}$ used is unlikely to be in error by more than 4 J K$^{-1}$ mol$^{-1}$, so that even allowing for errors in the observed values of $k_{16}$ and $k_{10}$, the combined enthalpies of formation of the allyl and the $HO_2$ radical will have to be increased by ca. 10 kJ mol$^{-1}$ for reaction (−16) to dominate the formation of $C_3H_6$. Sadly, such is the uncertainty over the thermochemistry of these radicals that such an upward revision is quite possible.

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