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Rate constants for the reaction of HO_2 radicals with cyclopentane and propane between 673 and 783 K

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Studies have been made of the separate addition of cyclopentane ($c\text{-}C_5H_{10}$) and propane (C_3H_8) to mixtures of O_2 and tetramethylbutane (TMB) between 673 and 783 K in aged boric-acid-coated vessels to obtain kinetic data for the reaction of HO_2 radicals with each of the additives. The contribution by OH radicals to the removal of $c\text{-}C_5H_{10}$ and C_3H_8 has been minimised by use of a total pressure of 15 Torr and by measurements well within 5% consumption of TMB and the additives. A full product analysis was carried out for each kinetic data point which shows that at least 85% of the radicals produced from $c\text{-}C_5H_{10}$ and C_3H_8 give conjugate alkene + HO_2 and which permits a precise correction for the small percentage of OH radicals formed. From measurements of the relative rates of consumption of TMB and the additives, values of $k_{12p}/k_7^{1/2}$ and $k_{12c}/k_7^{1/2}$ were obtained at each temperature used and were shown by sensitivity analysis to be relatively insensitive to any other parameter associated with the mechanism.

$$HO_2 + C_3H_8 \rightarrow H_2O_2 + C_3H_7 \tag{12p}$$

$$HO_2 + c\text{-}C_5H_{10} \rightarrow H_2O_2 + c\text{-}C_5H_9 \tag{12c}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{7}$$

Values of $E_{12p} - 1/2E_7 = 75.6 \pm 5.8$ kJ mol^{-1}, $\log[(A_{12p}/A_7^{1/2})/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^{1/2}] = 5.53 \pm 0.52$ and $E_{12c} - 1/2E_7 = 71.2 \pm 3.9$ kJ mol^{-1}, $\log[(A_{12c}/A_7^{1/2})/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^{1/2}] = 5.58 \pm 0.40$ were obtained which with $k_7 = 1.87 \times 10^9 \exp(-775/\text{T})$ dm^3 mol^{-1} s^{-1} give $E_{12p} = 78.8 \pm 6.6$ kJ mol^{-1}, $\log(A_{12p}/\text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}) = 10.17 \pm 0.57$ and $E_{12c} = 74.4 \pm 4.7$ kJ mol^{-1}, $\log(A_{12c}/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 10.22 \pm 0.45$. The parameters for reaction (12c) are in excellent agreement with $E = 73.2 \pm 5.0$ kJ mol^{-1}, $\log(A/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 10.23 \pm 0.49$ obtained in a previous study for the reaction of HO_2 radicals with cyclohexane. For use outside the temperature range of this study, the three-parameter function $k = AT^{2.5}\exp(-B/T)$ is recommended. From a combination of the data obtained for $c\text{-}C_5H_{10}$ and cyclohexane, values of $A = 7.9$ dm^3 mol^{-1} s^{-1} K$^{-2.5}$ and $B = 6970$ K are recommended for the abstraction by HO_2 radicals of a single secondary H atom from alkanes with a carbon number larger than 4. Use has been made of all the available data for HO_2 + alkane reactions to derive a data base for HO_2 attack at primary, secondary, and tertiary C–H sites in alkanes with an accuracy expressed as $\Delta\log = \pm 0.15$ between 600 and 800 K rising to ± 0.3 at 1200 K.

The importance of H abstraction from alkanes and related compounds by HO_2 radicals on mid-temperature combustion chemistry has been stressed in a recent publication[1] concerned with the kinetics of the HO_2 + cyclohexane reaction. The Arrhenius parameters presented therein are unique for abstraction from a secondary C–H bond. It has been argued[2] that the absence of strain energy in the ring results in the C–H bond dissociation energy in cyclohexane being the same to within 2–3 kJ mol^{-1} as that in linear alkanes. The question then arises as to the degree to which the cyclohexane kinetic data may be transferred for use with HO_2 + alkane. In order to provide an answer and further kinetic data for HO_2 abstraction reactions at secondary C–H bonds, experiments have been carried out with cyclopentane ($c\text{-}C_5H_{10}$) and propane as substrates between 673 and 783 K. Previous studies[3,4] have established that their oxidation chemistry in this region is simpler than that of cyclohexane, for example in particular that between 80 and 90% of the cyclopentyl and propyl radicals react with O_2 to give the conjugate alkene and an HO_2 radical, thus leaving only 10–20% to react *via* addition and decomposition to yield OH radicals. Compared with cyclohexyl + O_2, where only about 60% conjugate alkene is formed, the importance of OH radicals is therefore considerably reduced.

The decomposition of tetramethylbutane (TMB) in the presence of O_2 has again been used as a reliable and reproducible source of HO_2 radicals. Several studies[5,6] in both KCl- and aged boric-acid-coated Pyrex vessels have established that the decomposition proceeds in the initial stages *via* a very simple mechanism comprising reactions (1–11).

$$C_8H_{18} \rightarrow 2\ t\text{-}C_4H_9 \tag{1}$$

$$t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2 \tag{2}$$

$$HO_2 \rightarrow \text{surface} \tag{3}$$

$$HO_2 + C_8H_{18} \rightarrow H_2O_2 + C_8H_{17} \quad (4)$$

$$C_8H_{17} \rightarrow i\text{-}C_4H_8 + t\text{-}C_4H_9 \quad (5)$$

$$H_2O_2 \rightarrow \text{surface} \quad (6)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (7)$$

$$H_2O_2 + M \rightarrow 2OH + M \quad (8)$$

$$OH + C_8H_{18} \rightarrow H_2O + C_8H_{17} \quad (9)$$

$$t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8O + OH \quad (10)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (11)$$

In boric-acid-coated vessels, HO_2 and H_2O_2 are not destroyed at the surface so that $k_3 = k_6 = 0$. Further, as 99% of the t-C_4H_9 radicals react in reaction (2) to give HO_2 radicals, it is clear that the homolysis of H_2O_2 (reaction (8)) is effectively the only source of OH radicals, and the effect of this can be minimised by working at low total pressures (typically 15 Torr) and in the very early stages of reaction. By addition of CH_4[7], C_2H_6[8] and c-C_6H_{12}[1] to TMB + O_2 mixtures, Arrhenius parameters have been obtained for their reaction with HO_2 radicals. The fundamentals of the interpretation may be understood, with c-C_5H_{10} for example, by considering the simplest possible mechanism involving reactions (1), (2), (7), (12c), (13), and reaction (OP).

$$HO_2 + c\text{-}C_5H_{10} \rightarrow H_2O_2 + c\text{-}C_5H_9 \quad (12c)$$

$$c\text{-}C_5H_9 + O_2 \rightarrow c\text{-}C_5H_8 + HO_2 \quad (13)$$

$$c\text{-}C_5H_9 \rightarrow \text{other products} \quad (OP)$$

The relative rate of consumption of c-C_5H_{10} and TMB is given by eqn. (i).

$$d[c\text{-}C_5H_{10}]/d[TMB] = k_{12c}[c\text{-}C_5H_{10}]/(k_1k_7)^{1/2}[TMB]^{1/2} \quad (i)$$

The consumption of TMB may be measured directly from the yield of i-C_4H_8 (99%), and previous studies[4] have shown that *ca.* 80% of the c-C_5H_9 radicals undergo reaction (13) to give c-C_5H_8 and a regenerated HO_2 radical. Although a considerable improvement on the yields of c-C_6H_{10} + HO_2 of about 60% in the analogous reaction of c-C_6H_{11} radicals, a full product analysis is required for each kinetic datum point in order first to determine precisely the rate of consumption of c-C_5H_{10}, and secondly to monitor the loss of c-C_5H_{10} by reaction with OH radicals. As will be seen later, analysis confirms that the kinetic data obtained for the reactions of HO_2 radicals with c-C_5H_{10} and C_3H_8 are not particularly sensitive to the presence of OH radicals under the carefully chosen conditions of the present study.

Experimental

Details of the experimental procedure are given elsewhere.[1,5,6] Reactions were carried out in cylindrical Pyrex vessels, 20 cm in length and 5.2 cm in diameter. The aged boric-acid-coated surface was prepared to a totally reproducible state by carrying out repeated runs with $H_2 + O_2$ mixtures at 773 K.[9] Once established, the rate remained constant to within 1–2% over a period of years, and with correction for dead volume was totally independent of vessel diameter between 1.4 and 5.2 cm. Pressures were measured by transducer to better than 1% down to 0.1 Torr, and the temperature was controlled to better than 0.2 K along the length and breadth of the reaction vessel. At the very low rates involved, no temperature changes during reaction were detectable. The yields of products were measured by gas chromatography, and particular attention was given to establishing conditions for excellent peak resolution in order to achieve highly quantitative analyses. Electronic valves with response times of less than 0.1 s were used to admit the gases from the pre-mixing bulb and to sample the products at precise pre-selected time intervals. In practice, however, time is not a prime factor in the determination of precise kinetic data.

To avoid complications caused by secondary processes, when determining rate data the consumption of TMB and of the additives, c-C_5H_{10} or C_3H_8, was never allowed to exceed 5%, and was frequently significantly lower.

Experimental results

TMB + O_2 + c-C_5H_{10} mixtures

The yields of i-C_4H_8 (from TMB) and of the products from c-C_5H_{10} were measured over the first few % of reaction for several mixtures at 673, 713, 753, and 783 K. Pressures up to 4 Torr TMB and 2 Torr c-C_5H_{10} (not normally exceeded in order to facilitate good separation of the c-C_5H_{10} and c-C_5H_8 peaks) were used with added O_2 to a total pressure of 15 Torr, which maintained a very low level of homolysis of H_2O_2 (reaction (8)) to give OH radicals. Fig. 1 shows the product yields for the mixture containing 2, 2, and 11 Torr of TMB, c-C_5H_{10} and O_2, respectively at 753 K. As observed[1] with TMB + c-C_6H_{12} + O_2 mixtures, the product yields tend to increase autocatalytically due to the increased formation of OH radicals in reaction (8). At 673 K, however, the autocatalysis is effectively absent. Further, at all temperatures, the autocatalysis is less marked for i-C_4H_8 which is mostly formed through the homolysis of TMB, and as a consequence the relative rates of consumption of c-C_5H_{10} and TMB rise slightly with time. The initial product yields at 20 s, expressed as

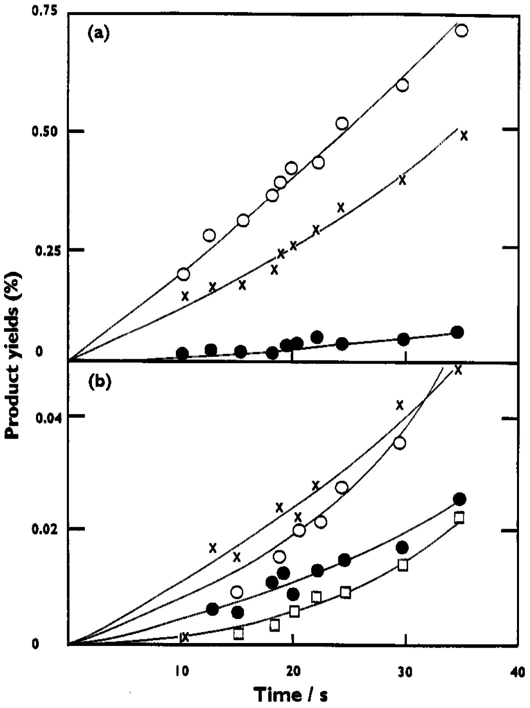

Fig. 1 Products from c-C_5H_{10} mixtures at 753 K. TMB = 2, c-C_5H_{10} = 2, O_2 = 11 Torr. (a) ○, i-C_4H_8; ×, c-C_5H_8; ●, 1,2-c-C_5H_8O. (b) ×, C_2H_4; ○, CO; ●, C_3H_6; □, c-pentadiene.

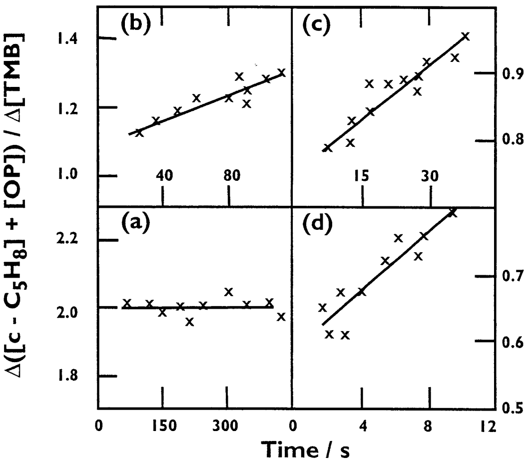

Fig. 2 Variation of $\Delta([c\text{-}C_5H_8] + [OP])/\Delta[TMB]$ with time at different temperatures. TMB = 4, $c\text{-}C_5H_{10} = 2$, $O_2 = 9$ Torr. (a), 673 K; (b), 713 K; (c), 753 K; (d), 783 K.

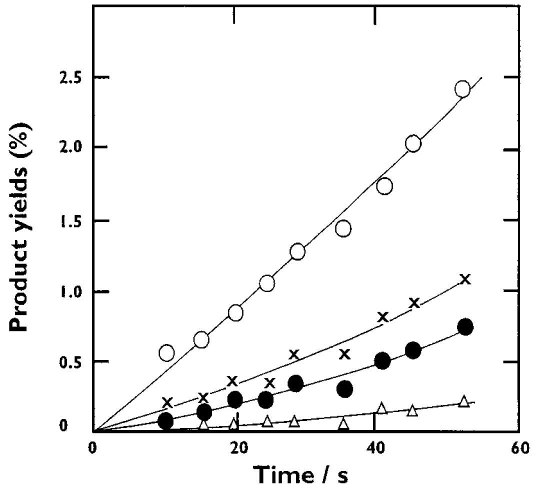

Fig. 3 Products from C_3H_8 mixtures at 753 K. TMB = 4, $C_3H_8 = 4$, $O_2 = 7$ Torr. ○, $i\text{-}C_4H_8$; ×, C_3H_6; ●, C_2H_4 (×4); △, C_3H_6O (×4).

absolute %, for the mixture TMB = 4, $c\text{-}C_5H_{10} = 2$, and $O_2 = 9$ Torr at 753 K are i-butene (1.01), $c\text{-}C_5H_8$ (0.365), C_2H_4 (0.0252), C_3H_6 (0.0095), 1,2-c-pentane oxide (0.0283), c-pentadiene (0.0065), $CH_2{=}CHCHO$ (trace, < 0,002), CO (0.0291). $i\text{-}C_4H_8$ is formed uniquely from TMB in yields of 99%,[5,6] and $c\text{-}C_5H_8$ in yields of 80–90% from $c\text{-}C_5H_{10}$. The yield of 1,2-cyclopentane oxide ($1,2\text{-}c\text{-}C_5H_8O$) is approximately 10%, in excellent agreement with that found when $c\text{-}C_5H_{10}$ is added to mixtures of $H_2 + O_2$ at 753 K and 500 Torr total pressure.[4] The yields of C_2H_4, CO, C_3H_6 and $CH_2{=}CHCHO$ all fall as the temperature is lowered, and small amounts of cyclopentadiene are observed, presumably formed very rapidly as a secondary product from $c\text{-}C_5H_8$. No other products were observed, but no analysis was made for HCHO. The consumption of TMB, with a 1% correction for the formation of isobutene oxide,[6,10] is monitored from the yield of $i\text{-}C_4H_8$, and that of $c\text{-}C_5H_{10}$ from the relationship $\Delta[c\text{-}C_5H_{10}] = \Delta[c\text{-}C_5H_8] + \Delta[OP]$, where $[OP] = [C_2H_4] + [1,2\text{-}c\text{-}C_5H_8O] + [c\text{-pentadiene}]$. Previous studies of $c\text{-}C_5H_{10}$ oxidation[4] and of allyl radical chemistry[11,12] under similar conditions indicate that $CH_2{=}CHCHO$, C_3H_6, and CO are formed in reaction sequences accompanying C_2H_4 (see later). If OH attack on $c\text{-}C_5H_{10}$ is ignored, then the value of $k_{12c}/k_7^{1/2}$ may be calculated directly from eqn. (i) because the value of k_1 is accurately known.[6]

Fig. 2 shows that the values of $\Delta([c\text{-}C_5H_8] + [OP])/\Delta[TMB]$ against time are invariant at 673 K, but increase noticeably at 783 K due to the enhanced effect of OH formation through H_2O_2 homolysis. Allowance for OH attack on $c\text{-}C_5H_{10}$ is made in two ways. First, the formation of OH radicals is calculated directly from the product profiles. With FENE defined as the fraction of $c\text{-}C_5H_9$ radicals which gives HO_2 radicals (effectively the fraction which gives $c\text{-}C_5H_8$), then 1 − FENE is the fraction giving OH radicals. At 673 and 713 K, the values of FENE are almost constant with mixture composition, but at 753 and 783 K are both smaller and sensitive to the pressure of O_2 due to the enhanced formation of C_2H_4 and its accompanying products. Despite this small complicating factor at the higher temperatures, the correction for OH attack on $c\text{-}C_5H_{10}$ is significantly less than required for the determination of $k(HO_2 + c\text{-}C_6H_{12})$ from related studies with $TMB + O_2 + c\text{-}C_6H_{12}$ mixtures.[1]

TMB + O_2 + C_3H_8 mixtures

Similar studies with very low consumptions were carried out with $TMB + O_2 + C_3H_8$ mixtures at 673, 723, and 753 K and a total pressure of 15 Torr. Fig. 3 shows the yields of $i\text{-}C_4H_8$ and of the C_3H_8 products for the mixture composition 4, 4, and 7 Torr of TMB, $c\text{-}C_5H_{10}$ and O_2 respectively at 753 K. Again there is little autocatalysis at 673 K, but it is noticeable at 753 K. Although small yields of oxetane were found as an initial product when C_3H_8 was added to $H_2 + O_2$ mixtures at 753 K,[3] in that environment the alkane is removed predominantly by the non-selective OH radical so the precursor of oxetane, $CH_3CH_2CH_2$, is formed in yields well in excess of 50%. In contrast, in the TMB study, C_3H_8 is consumed mostly by reaction with the highly selective HO_2 radical, so that the $CH_3CH_2CH_2$ radical is formed in relatively low yield. The CH_3CHCH_3 radical reacts with O_2 to give C_3H_6 and propene oxide in yields of 99% and 1%, respectively, and the $CH_3CH_2CH_2$ radical either forms C_3H_6 or propene oxide by reaction with O_2, or undergoes homolysis to give C_2H_4.[3] Consequently the consumption of C_3H_8 may be measured directly, in the absence of secondary reactions, by $\Delta[C_3H_8] = \Delta([C_3H_6] + [OP])$, where $[OP] = [C_2H_4] + [\text{propene oxide}]$. As in a related way with $c\text{-}C_5H_{10}$, the plots of $\Delta([C_3H_6] + [OP])/\Delta[TMB]$ are invariant with time at 673 K but increase slightly with time at the higher temperatures (see Table 5 further below).

Determination of rate constants for HO_2 + $c\text{-}C_5H_{10}$

The sub-mechanism, reactions (1)–(11), for TMB decomposition is given above, and the full mechanism for the initial stages[4] of $c\text{-}C_5H_{10}$ oxidation in Table 1. Handford-Styring and Walker[4] have shown that the isomerisation of $c\text{-}C_5H_9$ radicals is only of minor importance at 753 K and O_2 pressures above 50 Torr, but at the low O_2 pressures used here, the relative rate of reactions (13) and (16) would be about 10 : 1, consistent with the yields of C_2H_4 of about 10% at 753 K. Lodhi and Walker have studied the reactions of allyl radicals with HO_2[11] and with O_2,[11,12] and application of their data confirms that at the very high HO_2 concentrations in the TMB system effectively all allyl radicals will be removed in reactions (18) and (19). Homolysis of the peroxide bond in $CH_2{=}CHCH_2OOH$ gives OH radicals and the accompanying $CH_2{=}CHCH_2O$ radical gives either $CH_2{=}CHCHO$ (acrolein) [reaction (21)] or CO, HCHO, and HO_2, [reactions (22)–(24)]. Decomposition of the HCO radicals to give CO cannot compete under the present conditions.[13] The $H_2 + O_2 + c\text{-}C_5H_{10}$ studies[4] show that C_2H_4 is also formed with an OH radical in the overall sequence (25), although it is of minor importance at the low pressures of O_2 used here. The particularly important point that emerges is that in the initial stages of reaction each molecule of C_2H_4 formed is accompanied by an OH radical. As OH radicals are also formed in the overall reaction (15) which accounts for about 1% of the

Table 1 Sub-mechanism used for the determination of R_{12c}

$HO_2 + c\text{-}C_5H_{10} \rightarrow H_2O_2 + c\text{-}C_5H_9$	(12c)
$c\text{-}C_5H_9 + O_2 \rightarrow c\text{-}C_5H_8 + HO_2$	(13)
$OH + c\text{-}C_5H_{10} \rightarrow H_2O + c\text{-}C_5H_9$	(14)
$c\text{-}C_5H_9 + O_2 \rightarrow 1,2\text{-}c\text{-}C_5H_8O + OH$	(15)
$c\text{-}C_5H_9 \rightarrow \text{linear-}C_5H_9$	(16)
$\text{linear-}C_5H_9 \rightarrow C_2H_4 + CH_2CHCH_2$	(17)
$HO_2 + CH_2CHCH_2 \rightarrow C_3H_6 + O_2$	(18)
$HO_2 + CH_2CHCH_2 \rightarrow CH_2{=}CHCH_2OOH$	(19)
$CH_2{=}CHCH_2OOH \rightarrow CH_2{=}CHCH_2O + OH$	(20)
$CH_2{=}CHCH_2O + O_2 \rightarrow CH_2{=}CHCHO + HO_2$	(21)
$CH_2{=}CHCH_2O \rightarrow CH_2{=}CH + HCHO$	(22)
$CH_2{=}CH + O_2 \rightarrow HCHO + HCO$	(23)
$HCO + O_2 \rightarrow HO_2 + CO$	(24)
$c\text{-}C_5H_9 + O_2 \leftrightharpoons c\text{-}C_5H_9O_2 \rightarrow c\text{-}C_5H_8OOH \rightarrow$ $C_2H_4 + CH_2{=}CHCHO + OH$	(25)
$OH/HO_2 + c\text{-}C_5H_8 \rightarrow H_2O/H_2O_2 + c\text{-}C_5H_7$	(26)
$c\text{-}C_5H_7 + O_2 \rightarrow c\text{-}C_5H_6 + HO_2$	(27)

$c\text{-}C_5H_9$ radicals, the quantity 1 − FENE may be measured directly and precisely from the yields of C_2H_4 and $1,2\text{-}c\text{-}C_5H_8O$.

Use of a computer treatment is necessary, first to facilitate the incorporation of the parameters FENE and 1 − FENE into the interpretation, secondly to allow for the non-stationary formation of OH radicals from H_2O_2 homolysis, and thirdly to optimise the agreement between the experimental and calculated values of $\Delta[c\text{-}C_5H_{10}]/\Delta[\text{TMB}]$. Differential equations are written for reactants and products, and stationary state equations for the radicals. As previously, $[HO_2]$ is expressed in the form $G = k_7^{1/2}[HO_2]$, as it is the ratios $R_4 = k_4/k_7^{1/2}$ and $R_{12c} = k_{12c}/k_7^{1/2}$ that are directly involved in the computer interpretation. G is calculated from the stationary state equation for HO_2, and the Runge–Kutta numerical method used to solve the differential equations needed to predict the values of $\Delta[c\text{-}C_5H_{10}]/\Delta[\text{TMB}]$. A quantitative measure of the production of OH radicals is provided, as described above, by the parameter 1 − FENE, which is obtained from the detailed product analysis carried out for each kinetic point. Minor corrections, such as the allowance for 1% formation of OH radicals from $t\text{-}C_4H_9$ radicals [reaction (10)], are also carried out by the computer. The values of FENE and 1 − FENE are constant with time to within 3% over the very limited extent of reaction (< 5%) utilised for any particular mixture. With 1 − FENE measured precisely and $k_{10}/k_2 = 0.010$ between 673 and 783 K,[6] and k_1 known to better than 10%,[5] the other parameters required for the computer program are k_8, R_4, R_{12c}, k_{11}/k_9 and k_{14}/k_9. R_4 has been measured directly under the conditions used here[5,6] and k_{11}/k_9, of minor importance, is accurately known.[14] The value of $k_{14}/k_9 = 3.1 \pm 0.5$ at 753 K is obtained directly from $k_{14}/k(OH + H_2) = 24.6 \pm 3$ and $k_9/k(OH + H_2) = 8.0 \pm 0.9$ from separate studies of the addition of $c\text{-}C_5H_{10}$[4] and TMB[15] to $H_2 + O_2$ mixtures. Variation of k_{14}/k_9 with temperature is insignificant between 673 and 783 K, but is taken into account. The value of k_8 is accurately known[14] with $M = N_2$, O_2, and H_2, but the high proportions of TMB and $c\text{-}C_5H_{12}$ in the mixtures require relatively accurate values for a and b in eqn. (ii) for M_8, where 0.35, a, and b are the efficiencies of O_2, TMB, and $c\text{-}C_5H_{10}$, respectively, relative to that of H_2.

$$M_8 = 0.35[O_2] + a[\text{TMB}] + b[c\text{-}C_5H_{10}] \tag{ii}$$

A value of $a = 2.5$ gives an excellent fit to the TMB decomposition data in aged boric-acid-coated vessels[1,6] and $b = 2.0$, based on values for $c\text{-}C_6H_{12}$,[1] and C_2H_6[8] has been adopted for $c\text{-}C_5H_{10}$. The choice is not critical as will be seen from the sensitivity analysis.

The sole remaining parameter is R_{12c}, and the following procedure was adopted for its evaluation. A range of values was selected at each temperature and $\Delta[c\text{-}C_5H_{10}]/\Delta[\text{TMB}]$ calculated at three times all well within 5% consumption, and in some cases 1%, and then compared with the experimental values. The rms and mean deviations were calculated at each temperature, and the optimum values of R_{12c} isolated. As shown in Fig. 4, use of both deviations gives the same value. Table 2 compares the experimental and calculated values of $\Delta[c\text{-}C_5H_{10}]\Delta[\text{TMB}]$ at the three selected times, and gives the optimum values of R_{12c} obtained by use of the other parameters discussed above.

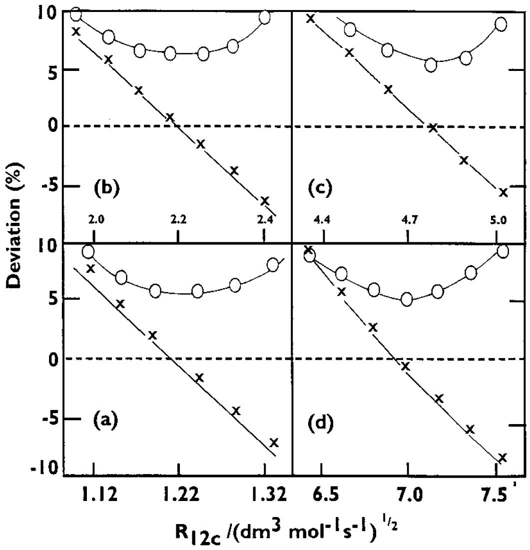

Fig. 4 Mean and rms deviations between observed and calculated values of $\Delta[c\text{-}C_5H_{10}]/\Delta[\text{TMB}]$. ×, mean deviation; ○, rms deviation. (a), 673 K; (b), 713 K; (c), 753 K; (d), 783 K.

Table 2 Calculated and observed values of $\Delta[c\text{-}C_5H_{10}]/\Delta[TMB]$

		Mixture composition			$\Delta[c\text{-}C_5H_{10}]/\Delta[TMB]$		
T/K	Time/s	TMB	$c\text{-}C_5H_{10}$	O_2	Obs.	Calc.	Optimum R_{12c}/ $(dm^3\ mol^{-1}\ s^{-1})^{1/2}$
673	120	4	4	7	3.98	3.78	1.22
	240				4.01	3.84	
	360				4.05	3.89	
	120	4	2	9	2.01	1.87	
	240				2.01	1.88	
	360				2.01	1.90	
	120	2	4	9	6.28	6.71	
	240				6.34	6.88	
	360				6.45	7.03	rms dev. = 6.8%
713	30	4	2	9	1.14	1.17	2.21
	60				1.18	1.20	
	90				1.25	1.22	
	30	2	2	11	2.04	1.96	
	60				2.13	2.01	
	90				2.30	2.07	
	30	4	1	10	0.580	0.578	
	60				0.605	0.589	
	90				0.639	0.601	
	30	1	2	12	2.87	3.19	
	60				3.13	3.28	
	90				3.24	3.37	rms dev. = 7.3%
753	10	4	2	9	0.803	0.841	4.77
	20				0.835	0.884	
	30				0.907	0.922	
	10	2	2	11	1.41	1.35	
	20				1.46	1.41	
	30				1.55	1.48	
	10	4	1	10	0.435	0.414	
	20				0.463	0.433	
	30				0.493	0.450	
	10	1	2	12	1.93	2.11	
	20				2.06	2.22	
	30				2.23	2.23	rms dev. = 6.1%
783	3	4	2	9	0.552	0.594	6.96
	6				0.620	0.634	
	9				0.687	0.672	
	3	2	2	11	0.902	0.912	
	6				1.02	0.969	
	9				1.13	1.02	
	3	4	1	10	0.292	0.293	
	6				0.304	0.313	
	9				0.330	0.331	
	3	1	2	12	1.29	1.38	
	6				1.40	1.46	
	9				1.57	1.54	rms dev. = 6.0%

The sensitivity analysis is summarised in Table 3 which shows the effect of a relatively large change of ±40% in each of the fixed parameters. The influences on R_{12c} are quite small under all conditions, and similar to those observed in the related study of $HO_2 + c\text{-}C_6H_{12}$,[1] with the exception that the importance of OH radicals is much reduced at low temperatures with $c\text{-}C_5H_{12}$. The values of R_{12c} are plotted in Arrhenius form in Fig. 5, and the optimum parameters $E_{12c} - 1/2\ E_7 = 71.2 \pm 3.9$ kJ mol^{-1} and $\log[(A_{12c}/A_7^{1/2})/(dm^3\ mol^{-1}\ s^{-1})^{1/2}] = 5.58 \pm 0.40$ are obtained, which may be compared with 70.0 ± 4.5 and 5.59 ± 0.41, respectively, for the reaction $HO_2 + c\text{-}C_6H_{12}$, the data for this reaction having been reinterpreted very slightly from the original.[1] Within experimental error both reactions have the same activation energy and A factor.

Determination of the rate constants for $HO_2 + C_3H_8$

The sub-mechanism used for the interpretation of the $TMB + O_2 + C_3H_8$ results is given in Table 4. As the yield of C_3H_6 (effectively equivalent to FENE) is about 90% and propene oxide (C_3H_6O), which is formed with an OH radical, is measured directly, the only uncertainty is the role of the CH_3 radicals formed in reaction (34). Consideration of the values of $k_{35} - k_{37}$ at 753 K shows that reaction (35) is their only important reaction. Baulch *et al.*[13] give $k_{35} = 2.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} between 300 and 2500 K and, from reviews by Westley *et al.*[16] and by Kerr and Moss,[17] respectively, $k_{36} = 1.0 \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_{37} = 6.5 \times 10^5$ dm^3 mol^{-1} s^{-1} at 753 K, so that with $[HO_2] = 5.0 \times 10^{-3}$ Torr at 10 s for the mixture TMB = 4, $C_3H_8 = 2$ and $O_2 = 9$ Torr, the rate of reaction (35) relative to the combined rates of reactions (36) and (37) is about 20. Arising from compensating factors the relative rate changes little for all conditions used. It should be further noted that the termolecular reaction $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ cannot compete at the low O_2 and total pressures used here. It may be concluded that the formation of C_2H_4 in (34), only a minor reaction anyway, is accompanied by an OH radical. In confirmation, no CH_4 could be detected in the initial products, even at 673 K where the relative rates of (36) and (37) are slightly higher. Nevertheless, the computer program makes the very small corrections (<1% effect on R_{12p}).

Table 3 Summary of sensitivity analysis for R_{12c}

		% change in R_{12c}			
Parameter changed	% change	783 K	753 K	713 K	673 K
k_1	+40%	+7.8	+6.8	+5.7	+3.5
	−40%	−8.4	−7.3	−6.3	−4.2
k_{10}/k_2	+40%	−0.4	0.0	−0.2	0.0
	−40%	+0.3	+0.4	+0.1	0.0
k_8	+40%	−3.0	−1.4	−1.2	−0.8
	−40%	+3.0	+2.3	+1.0	+0.8
k_{14}/k_9	+40%	−2.9	−2.8	−2.4	−2.2
	−40%	+3.5	+3.4	+3.0	+3.3
FENE	To maximum[a]	+7.9	+6.3	+5.1	+1.5
	−40%	−11.0	−9.0	−6.5	−1.5

[a] Raised to maximum value of unity from values ranging between about 0.8–0.9.

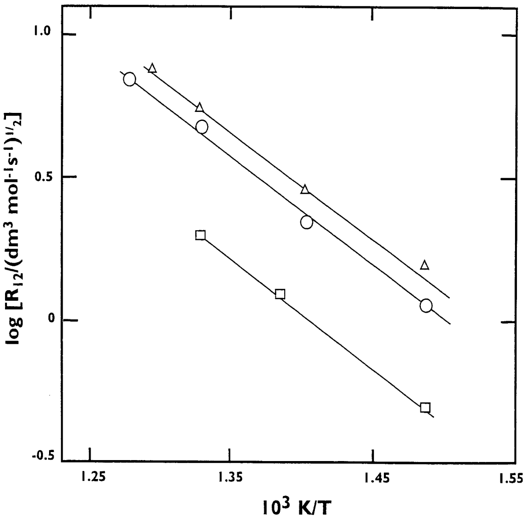

Fig. 5 Arrhenius plots for R_{12c} and R_{12p} between 673 and 783 K. □, R_{12p} (for C_3H_8); ○ R_{12c} (for $c\text{-}C_5H_8$); Δ, R_{12} (for $c\text{-}C_6H_{12}$ from ref. 1).

The results were interpreted by computer, as described for $c\text{-}C_5H_{10}$. The values of FENE increased slightly with temperature because of the greater importance of reaction (34), but were never below 0.90. Consequently, the importance of OH radicals in removing C_3H_8 was significantly less than in the consumption of both $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{10}$.[1] A value

Table 4 Sub-mechanism used for the determination of R_{12p}

$HO_2 + C_3H_8 \rightarrow H_2O_2 + CH_3CH_2CH_2/CH_3CHCH_3$	(12p)
$OH + C_3H_8 \rightarrow H_2O + CH_3CH_2CH_2$	(29a)
$OH + C_3H_8 \rightarrow H_2O + CH_3CHCH_3$	(29b)
$CH_3CHCH_3 + O_2 \rightarrow C_3H_6 + HO_2$	(30)
$CH_3CH_2CH_2 + O_2 \rightarrow C_3H_6 + HO_2$	(31)
$CH_3CHCH_3 + O_2 \rightarrow C_3H_6O + OH$	(32)
$CH_3CH_2CH_2 + O2 \rightarrow C_3H_6O + OH$	(33)
$CH_3CH_2CH_2 + M \rightarrow CH_3 + C_2H_4 + M$	(34)
$CH_3 + HO_2 \rightarrow CH_3O + OH$	(35)
$CH_3 + C_3H_8 \rightarrow CH_4 + CH_3CH_2CH_2/CH_3CHCH_3$	(36)
$CH_3 + C_8H_{18} \rightarrow CH_4 + C_8H_{17}$	(37)

of $k_{29}/k_9 = 1.24 \pm 0.2$ was obtained at 753 K from [18] $k_{29}/k(OH + H_2) = 9.9 \pm 1.2$ and[15] $k_9/k(OH + H_2) = 8.0 \pm 0.9$. The relative efficiency b of C_3H_8 as M in reaction (8) is taken as 2 and applied through eqn. (ii). The values of R_{12p} were optimised using the same procedure as for R_{12c} from the c-C_5H_{10} results. Fig. 6 shows that the rms and mean deviations give the same optimum values of R_{12p}, and Table 5 compares the experimental and calculated values of $\Delta[C_3H_8]/\Delta[TMB]$ at the selected times where consumption barely exceeded 1%. The sensitivity analysis, summarised in Table 6, shows that the optimum values of R_{12p} are insensitive to all the fixed parameters. Although a 40% reduction in FENE would reduce R_{12p} by about 10%, FENE and 1 − FENE are measured to better than 10% so that the likely error is less than 3%. The values of R_{12p} are plotted in Fig. 5 and over the range 673–753 K, $E_{12p} - 1/2E_7 = 75.6 \pm 5.8$ kJ mol^{-1} and $\log[(A_{12p}/A_7{}^{1/2})/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^{1/2}] = 5.53 \pm 0.52$. A higher activation energy for the reaction of HO_2 radicals with C_3H_8 is understandable, when compared with those for c-C_5H_{10} and c-C_6H_{12}, because of the presence of primary C–H bonds in C_3H_8.

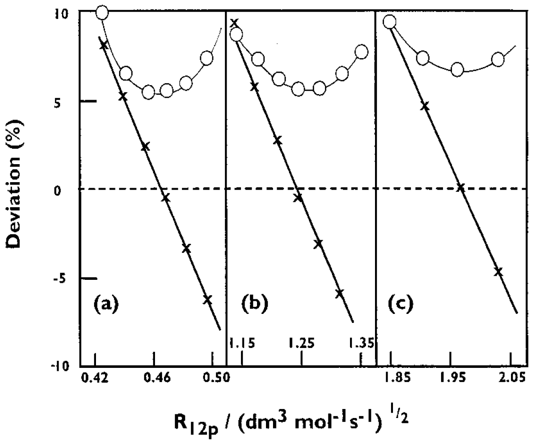

Fig. 6 Mean and rms deviations between observed and calculated values of $\Delta[C_3H_8]/\Delta[TMB]$. ×, mean deviation; ○, rms deviation. (a), 673 K; (b), 723 K; (c), 753 K.

Table 5 Calculated and observed values of $\Delta[C_3H_8]/\Delta[TMB]$

		Mixture composition			$\Delta[C_3H_8]/\Delta[TMB]$		
T/K	Time/s	TMB	C_3H_8	O_2	Obs.	Calc.	Optimum R_{12p}/(dm^3 mol^{-1} s^{-1})$^{1/2}$
673	300	4	4	7	1.49	1.47	0.468
	600				1.49	1.49	
	900				1.49	1.51	
	300	2	4	9	2.68	2.58	
	600				2.73	2.66	
	900				2.76	2.72	
	300	1	4	10	4.33	4.46	
	600				4.45	4.65	
	900				4.50	4.87	
	300	4	1	10	0.342	0.362	
	600				0.342	0.364	
	900				0.342	0.366	rms dev. = 4.7%
723	50	4	5	6	1.29	1.34	1.24
	100				1.38	1.40	
	150				1.50	1.49	
	50	4	2	9	0.485	0.526	
	100				0.521	0.558	
	150				0.585	0.597	
	50	2	5	8	2.46	2.24	
	100				2.59	2.42	
	150				2.76	2.65	rms dev. = 5.9%
753	15	4	4	7	0.780	0.762	1.96
	30				0.871	0.820	
	45				0.943	0.869	
	15	2	4	9	1.23	1.21	
	30				1.34	1.31	
	45				1.45	1.38	
	15	1	4	10	1.74	1.88	
	30				1.88	2.06	
	45				2.04	2.23	rms dev. = 6.5%

Table 6 Summary of sensitivity analysis for R_{12p}

		% change in R_{12p}		
Parameter changed	% change	753 K	723 K	673 K
k_1	+ 40	+ 6.8	+ 5.9	+ 4.2
	− 40	− 8.1	− 6.4	− 4.6
k_{10}/k_2	+ 40	− 0.2	− 0.2	− 0.0
	− 40	+ 0.2	+ 0.1	+ 0.0
k_8	+ 40	− 3.2	− 2.8	− 0.8
	− 40	+ 2.2	+ 1.6	+ 0.7
k_{29}/k_9	+ 40	− 3.2	− 2.3	− 1.3
	− 40	+ 4.0	+ 3.3	+ 1.8
FENE	To maximum[a]	+ 4.5	+ 2.9	+ 0.4
	− 40	− 8.3	− 3.4	− 0.7

[a] Raised to maximum value of unity from about 0.9.

Absolute values of k_{12c} and k_{12p}

The absolute values of k_{12c} and k_{12p}, calculated from the ratios by use[13] of $k_7 = 1.87 \times 10^9\exp(-775/T)$ dm^3 mol^{-1} s^{-1}, are given in Table 7, together with the Arrhenius parameters and

Table 7 Absolute values[a] of rate constants

T/K	k_{12p}	k_{12c}	$k(HO_2 + c\text{-}C_6H_{12})^1$
673	1.14×10^4	2.95×10^4	3.79×10^4
713	—	5.55×10^4	7.25×10^4
723	3.14×10^4	—	—
753	5.07×10^4	1.23×10^5	1.44×10^5
773	—	—	1.97×10^5
783	—	1.84×10^5	—
log(A/dm^3 mol^{-1} s^{-1})	10.17 ± 0.52	10.22 ± 0.45	10.23 ± 0.49[b]
E/kJ mol^{-1}	78.8 ± 6.6	74.4 ± 4.7	73.2 ± 5.0[b]

[a] dm^3 mol^{-1} s^{-1} units; accuracy *ca.* ± 10%. [b] Small re-interpretation of original data.[1]

the data determined for $HO_2 + c\text{-}C_6H_{12}$ over a similar temperature range.[1] Although the values of k_{12p} lie below those of k_{12c} and $k(HO_2 + c\text{-}C_6H_{12})$, when allowance is made through the additivity rule for the presence of 6 primary C–H bonds by use[8] of $k(HO_2 + C_2H_6) = 10^{10.13}\exp(-10330/T)$ dm^3 mol^{-1} s^{-1}, the Arrhenius plot in Fig. 7 shows that on a per C–H bond basis, the values of the rate constant for reaction at the secondary C–H bonds in C_3H_8 lie consistently about 45% above those for $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{12}$. The data for the cyclic compounds agree extremely well, however, with $E = 73.9$ kJ mol^{-1} and log[A(per C–H bond)/(dm^3 mol^{-1} s^{-1})] = 9.15. For a secondary C–H bond in C_3H_8, the data yield 76.1 and 9.53, respectively.

Use of the bond-additivity rule for H/OH + alkanes with a low carbon number has been questioned by Cohen[19,20] mainly because the entropy of activation per carbon atom, calculated by transition state theory, is not constant until C_n reaches 5. In an alternative bond additivity approach Atkinson[21] has allowed for the effect of near-neighbour groups by giving expressions which effectively modify the activation energy of the reaction. Although the use of $k(HO_2 + C_2H_6)$ to allow for attack at the primary C–H bonds in C_3H_8 may introduce a small error, if the difference in the quoted[22] values of $D(C_2H_5\text{–}H) = 423.0 \pm 1.6$ kJ mol^{-1} and $D(CH_3CH_2CH_2\text{–}H) = 420.0 \pm 2.5$ kJ mol^{-1} s^{-1} is taken as 3 kJ mol^{-1}, then $E(HO_2 + C_2H_6) - E(HO_2 + \underline{CH_3}CH_2\underline{CH_3})$ ~1.5 kJ mol^{-1} the effect of which at 753 K effectively cancels out that caused by the estimated difference of about 2 J K^{-1} mol^{-1} in the entropies of activation.

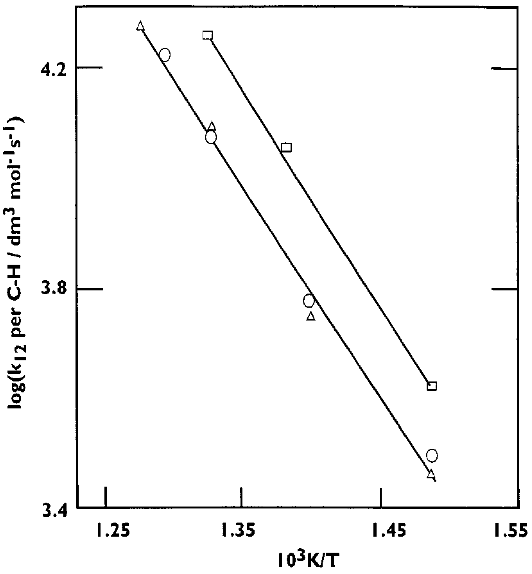

Fig. 7 Arrhenius plots for k_{12} per secondary C–H bond in C_3H_8, $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{12}$. O, $c\text{-}C_6H_{12}$ (ref. 1); Δ, $c\text{-}C_5H_{10}$; □, C_3H_8 (after allowance for primary attack–see text).

Accepting that the values for $k(HO_2 + CH_3\underline{CH_2}CH_3)$ are accurately placed on a per C–H bond basis at about 45% above those for attack at the CH_2 positions in $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{12}$, it is important to establish the validity of the data for modelling purposes. Although values of $D(c\text{-}C_5H_9\text{–}H) = 403.5 \pm 2.5$ kJ mol^{-1} and $D(c\text{-}C_6H_{11}\text{–}H) = 399.6 \pm 4$ kJ mol^{-1}, compared with $D[(CH_3)_2CH\text{–}H] = 412 \pm 1.6$ kJ mol^{-1}, have been quoted recently,[22] those for the cyclic alkanes were determined when much lower values were considered 'established' for C–H bond dissociation energies in alkanes.[23] Given that there is effectively zero strain energy in the rings, then the C–H bond dissociation energies in $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{12}$ should differ by no more than 2 kJ mol^{-1} from that for the secondary C–H bonds in C_3H_8, as strongly argued by McMillen and Golden.[23] Their view will be accepted here and

Table 8 Kinetic data for HO_2 + alkanes in the form $k = AT^{2.5}\exp(-B/T)$

Alkane	Range/K	A/dm^3 mol^{-1} s^{-1} K$^{-2.5}$	B/K	Ref.	Note
CH_4 (total)	716	47	10570	7	a
C_2H_6 (total)	673–793	71	8480	8	b
(per primary C–H)	673–793	11.8	8480	8	b
Tetramethylbutane (total)	673–793	109	8395	6	b
(per primary C–H)	673–793	6.0	8395	6	b
$c\text{-}C_6H_{12}$ (total)	673–773	77	6800	1	b
(per secondary C–H)	673–773	6.4	6800	1	b
$c\text{-}C_5H_{10}$ (total)	673–783	97	7130	Present	b
(per secondary C–H)	673–783	9.7	7130	Present	b
$c\text{-}C_6H_{12}$ + $c\text{-}C_5H_{10}$ combined (per secondary C–H)	673–783	7.9	6970	Present	b
C_3H_8 (total)	673–753	99	7760	Present	b
(per secondary C–H)	673–753	24.5	7480	Present	b c
$i\text{-}C_4H_{10}$ (total)	753	$k = 8.7 \times 10^4$		26	d
(per tertiary C–H)	753	15.0	6170	26	c e
2,3-dimethylbutane (total)	753	$k = 1.23 \times 10^5$		27	d
(per tertiary C–H)	753	10.0	6100	27	e f
HCHO (total)	540–1600	40.8	5135	24	g
(per aldehydic C–H)	540–1600	20.4	5135	24	

[a] Two-thirds of the total A factor for C_2H_6 assumed. [b] Obtained from fit to data [c] Additivity rule used with C_2H_6 data. [d] Units of rate constant, dm^3 mol^{-1} s^{-1}. [e] A factor assumed, based on other values. [f] Additivity rule used with tetramethylbutane data. [g] Based on 4 independent studies, see ref. 24.

if so there must be a further factor contributing to the difference in the rate constants. As the entropy of activation per C–H bond for HO_2 attack on c-C_5H_{10} and c-C_6H_{12} will not differ significantly, the congruity of the rate constants per CH_2 group is predictable. The higher rate constant for the secondary CH_2 group in C_3H_8 probably therefore arises at least partially from a lower (negative) value for the entropy of activation. The precise difference is difficult to estimate, but lies in the region of 4–8 J K^{-1} mol^{-1}, which implies that HO_2 attack at the CH_2 site in C_3H_8 would be a factor 1.5–2.5 faster than for c-C_5H_{10} and c-C_6H_{12}, compared with the figure of 1.45 observed experimentally. Further discussion at this stage is premature in the absence of more experimental data.

Based on the Arrhenius expression, values of A(per C–H bond) = 3.0×10^9 dm^3 mol^{-1} s^{-1} and $E = 75$ kJ mol^{-1} are recommended for HO_2 attack at the CH_2 groups in C_3H_8 and C_4H_{10} between 650 and 800 K, with A(per C–H bond) reduced to 1.5×10^9 dm^3 mol^{-1} s^{-1} for alkanes where the carbon number exceeds 4. Outside this temperature range use of the expression $k = AT^{2.5}\exp(-B/T)$ is preferred, given the clear evidence of non-Arrhenius behaviour over large temperature ranges for many radical reactions, the value of $k = 4.1 \times 10^{1} T^{2.5}\exp(-5136/T)$ dm^3 mol^{-1} s^{-1} determined experimentally[24] over the range 540–1600 K for $HO_2 + HCHO$, and application of Bozzelli's[25] methods which suggests that n lies between 2.2 and 3.0. Table 8 summarises all the available data in this form. The values of B fall consistently as the HO_2 reactions approach approximate thermoneutrality ($HO_2 + HCHO$). The non-Arrhenius A factors per C–H bond fall in the range 6.5–25 dm^3 mol^{-1} s^{-1} $K^{-2.5}$ and, although perhaps fortuitously, are consistent with Cohen's[19,20] view that in abstractions by radicals such as H and OH the entropy of activation per C–H bond does not become constant until the alkane has a carbon number exceeding 4. The accuracy of the rate constants in the database may be expressed in the form $\Delta \log k = \pm 0.15$ between 600 and 800 K rising to ± 0.3 at 1200 K.

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