

# ***n*-Propylcyclohexane lean oxidation and autoignition at low temperatures and elevated pressures**

M. Crochet, G. Vanhove\*, M. Ribaucour, R. Minetti

Physico-Chimie des Processus de Combustion et de l'Atmosphère, UMR CNRS 8522  
Université des Sciences et Technologies de Lille, Bâtiment C11, 59655 Villeneuve d'Ascq, Cedex, France

## **Abstract**

The autoignition of *n*-propylcyclohexane is studied in a rapid compression machine over the pressure range 4.5-13.4 bar, between 620 and 930 K, and for three equivalence ratios  $\phi$ : 0.3, 0.4, and 0.5. Two-stage ignitions are observed at the lowest pressures between 620 and 750 K. A negative temperature coefficient region is present at the lowest pressures for  $\phi = 0.5$  and 0.4. Chemical analyses are also performed and 47 oxidation products are identified in a sample withdrawn from the combustion chamber. The production of most of them is explained according to the low-temperature oxidation chemistry of the *n*-propylcyclohexane.

## **Introduction**

The Homogeneous Charge Compression Ignition (HCCI) combustion process is an interesting alternative to the conventional Spark Ignition (SI) and Compression Ignition (CI) processes. Its advantages are high combustion efficiency as in CI combustion and low emissions of NO<sub>x</sub> and particulate matter as in SI combustion. Its disadvantages are high hydrocarbon and carbon monoxide emissions, difficulty in starting and controlling the combustion. One requirement of the HCCI combustion process is the use of a low equivalence ratio of the fuel/air mixture (between 0.2 and 0.5) to avoid extreme pressure rise rates during the autoignition of the mixture and hence mechanical stress and noise. The NADI (Narrow Angle Direct Injection) concept [1] suggests a combined operating mode for CI engines: Part-time diesel for high loads and part-time HCCI for light loads.

In the context of the development of the HCCI engine technology, there is need for efficient kinetic modelling of the oxidation chemistry of potential fuels to develop predictive tools of the autoignition in the complex engine environment. Experimental studies are therefore required for means of validation. The rapid compression machine (RCM) in Lille is the ideal experimental device for such studies: it offers pressure and temperature ranges close to those reached at the end of the compression in a HCCI engine, as well as constant volume and sampling possibility during the ignition delay.

This paper explores the autoignition and oxidation in an engine environment of a molecule of particular interest for surrogate diesel fuels [2]: *n*-propylcyclohexane. Previous works on cyclanes low-temperature oxidation have shown the importance of the bicyclic transition states on the isomerization steps [3,4].

## **Experimental**

Autoignition experiments were conducted in a rapid compression machine (RCM) which compression ratio was fixed at 9.5. A detailed description of this RCM and the experimental procedure can be found elsewhere [5,6]. Several *n*-propylcyclohexane/O<sub>2</sub>/inert mixtures with different inert composition were compressed. The top dead centre (TDC) temperature  $T_c$  was varied by changing the composition of the diluent so that the heat capacity of the mixture was changed. Some or all N<sub>2</sub> was replaced by Ar and CO<sub>2</sub> to reach higher and lower temperatures.  $T_c$  is calculated according to the adiabatic core gas model [5] using the initial pressure  $P_0$ , the initial temperature  $T_0$ , the measured pressure at TDC  $P_{TDC}$ , and the temperature dependence of the ratio of specific heats  $\gamma$ .

Three values of  $P_0$  were used (250, 350, and 500 torr) leading to a full range of 4.5-13.4 bar for  $P_{TDC}$ . The covered range for  $T_c$  was 620-930 K. Three equivalence ratios were used:  $\phi = 0.3, 0.4,$  and  $0.5$ . The ratio [O<sub>2</sub>]/[inert] was equal to 0.27, the same as in air. *n*-Propylcyclohexane being weakly volatile, the gas mixtures were prepared in glass vessels heated at 353 K and the value of  $T_0$  was 363 K.

For each experiment, pressure and light emission signals were recorded. Fig. 1 shows an example of these signals in the case of a two-stage autoignition. The cool flame delay time is measured from TDC to the maximum of the first peak of light emission. The ignition delay time is measured from TDC to the point of crossing of two lines: one line is tangent to the portion of the pressure signal marked by the pressure rise associated to ignition, the other is tangent to the portion of the pressure signal before the pressure rise as shown on Fig. 1. This procedure was used because the pressure rise was often not sharp due to the low equivalence ratio.

Chemical analyses were also performed to identify the stable oxidation products formed during

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\* Corresponding author: guillaume.vanhove@univ-lille1.fr  
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the delay. A sampling system was used to quench and collect the reacting mixture at a selected time between the cool flame and ignition. The collected mixture was analysed by gas chromatography coupled with mass spectrometry. The constituents were separated with a 50 m 5% phenylmethylsilicone capillary column (HP5) and identified on the basis of their mass spectrum.

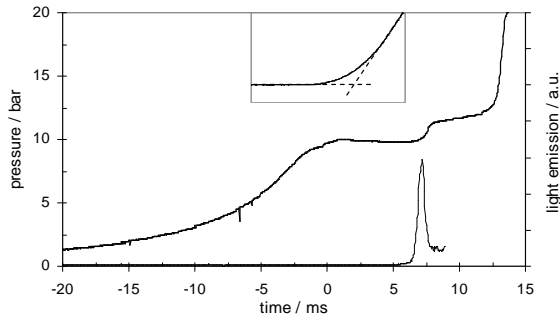


Fig. 1. Pressure (upper curve) and light emission signal (lower curve) versus time for a two-stage autoignition at  $T_c = 663$  K,  $P_{TDC} = 9.7$  bar,  $\phi = 0.5$ . Window: Measurement of the ignition delay time.

## Results and discussion

### Phenomenology of ignition

Fig. 2 pictures the influence of  $\phi$  and  $P_0$  on the evolution of ignition delay time versus  $T_c$ . For  $\phi = 0.5$  (Fig. 2a), the ignition limit ( $T_1$ ), which is the lowest temperature at which ignition occurs, is clearly identified for all  $P_0$ :  $T_1 = 620$  K for  $P_0 = 500$  and 350 torr, and  $T_1 = 630$  K for  $P_0 = 250$  torr. When  $T_c$  is increased, a negative temperature coefficient (NTC) zone is observed in the range 670-750 K for  $P_0 = 250$  torr. For  $P_0 = 350$  torr, only a change in the slope of the delay time curve decrease is visible in the range 680-750 K.

Overall, the delay time increases when  $\phi$  or  $P_0$  is decreased but above 875 K the delay times are close. At  $\phi = 0.4$  (Fig. 2b), ignition limit ( $T_1$ ) is close to 630 K for  $P_0 = 500$  and 350 torr, and close to 650 K for  $P_0 = 250$  torr. The NTC zone is not well marked for the highest initial pressures, however it is clearly identified for  $P_0 = 250$  torr between  $T_c = 680$  and 750 K. The temperature range in which the NTC is observed does not vary so much with  $\phi$  but its amplitude is very different: 20 ms at  $\phi = 0.5$  and 70 ms in that case at  $\phi = 0.4$ .

Fig. 2c shows the evolution of ignition delay time versus  $T_c$  for  $\phi = 0.3$ . At  $P_0 = 250$  torr, *n*-propylcyclohexane/“air” mixtures do not autoignite below  $T_c = 800$  K. The NTC zone is not as well marked as in the case of the experiments at higher equivalence ratios, but we can note a change in the slope of the delay time decrease in the range 810-820 K. When  $P_0$  is increased,  $T_1$  is decreased and is close to 700 K and 640 K for  $P_0 = 350$  and 500 torr, respectively.

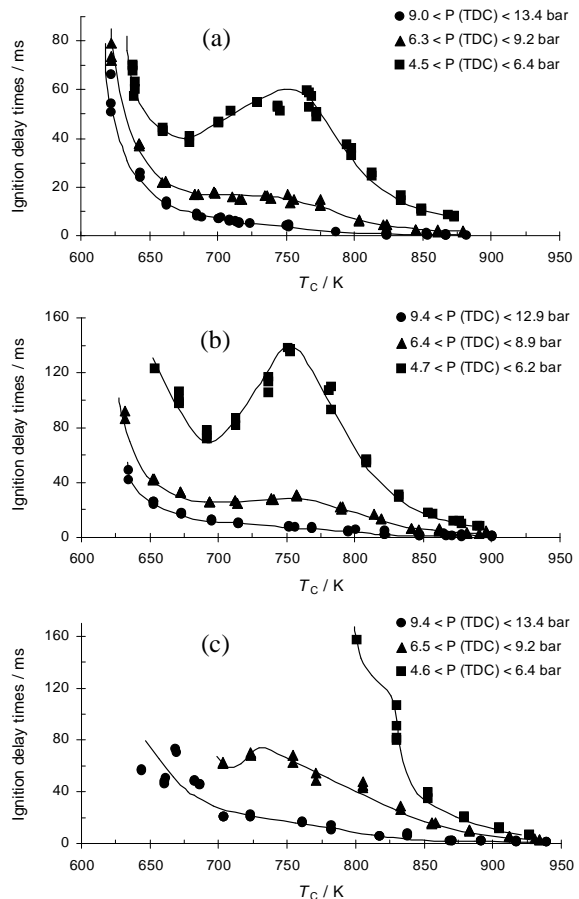


Fig. 2. Ignition delay times versus  $T_c$  at different initial pressures.  $P_0 = 500$  torr ( $\bullet$ ), 350 torr ( $\blacktriangle$ ), 250 torr ( $\blacksquare$ ).  $\phi = 0.5$  (a), 0.4 (b), 0.3 (c)

In Fig. 2a, there is between  $T_c = 730$  and 770 K for  $P_0 = 250$  torr, a particular behaviour which suggests a three-stage ignition with a double NTC zone. At these temperatures, cool flame delay times are very short (Fig. 5) and it is not possible to assure that we have a periodic cool flame as it was observed in an HCCI engine [7]. However, we can note that a similar phenomenology was observed with another cyclic molecule, the cyclohexane, which has been studied in RCM [8] as it can be seen on Fig. 3. Further ignition results with other alicyclic molecules are needed to allow a correct interpretation.

In Fig. 2c, we can observe a strong dispersion of experimental measurements at low temperatures from  $T_c = 640$  to 680 K, at  $\phi = 0.3$  and  $P_0 = 500$  torr. In these conditions, the hydrocarbon molar fraction does not represent more than 0.5% of the mixture. To reach low core-gas temperatures, we substitute the nitrogen by carbon dioxide to increase the calorific capacity of the initial mixture. The thermic effect of the inert gas on ignition delay times is well known but the kinetic effect is not. This can explain the combustion instabilities observed when we reach the ignition limit  $T_1$ .

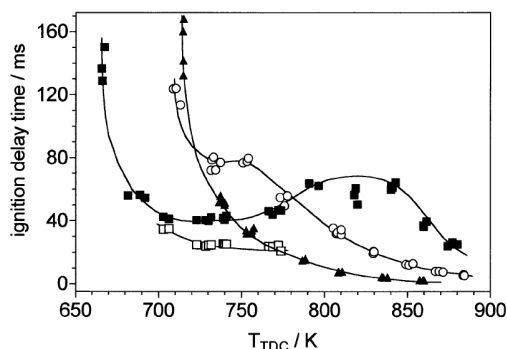


Fig. 3. Ignition and cool flame delay times of hydrocarbon/O<sub>2</sub>/inert mixtures versus  $T_c$ .  $P_0 = 350$  torr,  $\phi = 1$ , dilution as in air,  $P_{TDC} = 7$  to 9 bar. Cyclohexane (■); cyclohexene (○); cyclohexa-1,3-diene (▲); cool flame delay times of cyclohexane (□) [8].

Figs. 4 and 5 show the evolution of cool flame delay times versus  $T_c$  at different equivalence ratios and initial pressures. One can note that the cool flame delay times decrease when  $T_c$  increases and is very weakly influenced by  $\phi$  or  $P_0$  in the range 0.3-0.5 and 4.5-10.3 bar respectively.

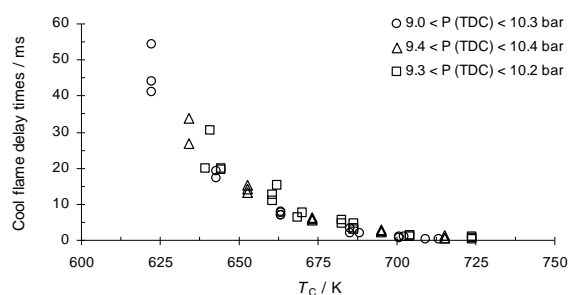


Fig. 4. Cool flame delay times versus  $T_c$  at different equivalence ratios.  $\phi = 0.5$  (○), 0.4 (Δ), 0.3 (□).  $P_0 = 500$  torr.

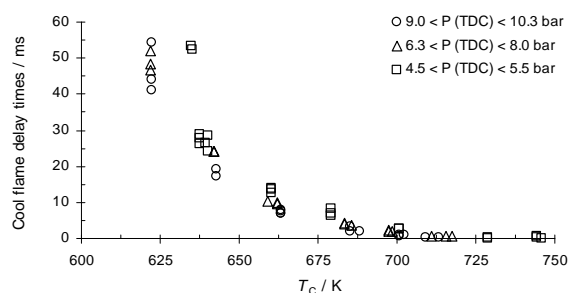


Fig. 5. Cool flame delay times versus  $T_c$  at different initial pressures.  $P_0 = 500$  torr (○), 350 torr (Δ), 250 torr (□).  $\phi = 0.5$ .

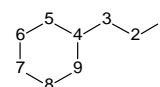
### Reaction pathways producing the oxidation products

The chemical analysis was performed in the following conditions:  $T_c = 670$  K,  $P_{TDC} = 6.5$  bar,  $\phi = 0.5$ . The sample was taken at 17 ms after TDC. The

names of the major identified species are listed in Table 1. The identification of the various products was complicated because of some peaks overlapping and cis/trans isomerism of unsaturated compounds.

Another difficulty arose from a lack of reference spectra for epoxy compounds of *n*-propylcyclohexane. Nevertheless, a careful inspection of the electron impact fragmentation spectra enabled to recognize the size and position of most of the O-heterocycles thanks to specific fragmentation paths: the molecular ions undergo transannular fragmentations leading to stable small molecules and an odd-electron fragment ion of low mass number. From the areas of the peaks of GC/MS chromatogram the major oxidation products are propenal, propanal, cyclohexene, methylene-cyclohexane, cyclohexanone, propyl-4-cyclohexene, propyl-3-cyclohexene and cyclohexanespiro-(ethyl-2-ox-2-irane). Neon was used as an internal standard in the initial mixture and measured after reaction in order to express the concentration of products in percentage of carbon atoms and the selectivities of the species expressed in carbon atoms per 100 carbon atoms of *n*-propylcyclohexane consumed (Table 1).

The oxidation scheme of *n*-propylcyclohexane was built by applying the low-temperature oxidation reaction scheme of alkanes. For the convenience of the discussion, the carbon atoms of *n*-propylcyclohexane are numbered as follows:



The abstraction of an H atom from *n*-propylcyclohexane by the pool of radicals forms seven propylcyclohexyl radicals  $R_1^\bullet$ . The reversible addition of O<sub>2</sub> to each radical  $R_1^\bullet$  leads to seven propylcyclohexylperoxy radicals  $R_1O_2^\bullet$ . The formation of the radical  $R_1O_2^\bullet$  is shown on Fig. 6.

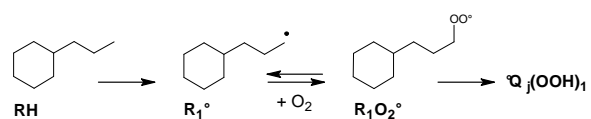





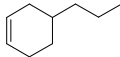
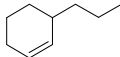
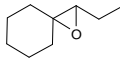


Fig. 6. Formation of the propylcyclohexylperoxy radical  $R_1O_2^\bullet$ .

The radicals  $R_1O_2^\bullet$  undergo an internal H-atom transfer to produce a radical  $^{\circ}Q_j(OOH)_i$ , in which Q is C<sub>9</sub>H<sub>17</sub>, the subscript *i* indicates the position of the OOH function and the subscript *j* the position of the radical centre. All QOOH radicals can form an O-heterocycle and OH by an O-O bond scission followed by a cyclization (product n° 45). They can also add O<sub>2</sub> to form  $^{\circ}O_2QOOH$  radicals, which can undergo an internal H-atom transfer and an O-O bond scission to form a ketohydroperoxide and OH. The formation of a conjugate alkene (products n° 33, 36) and HO<sub>2</sub> after a C-O bond breaking is only possible for  $\alpha$ -QOOH radicals, which are of type  $^{\circ}Q_{i+1}(OOH)_i$  or  $^{\circ}Q_{i-1}(OOH)_i$  as shown on Fig. 7.

**Table 1**

Major products identified in the low temperature oxidation of *n*-propylcyclohexane, % C, and selectivity (see text) in C per 100 C consumed. Each product is numbered according to its time of elution on a HP5 column.  $T_c = 670$  K,  $P_{TDC} = 6.5$  bar,  $\phi = 0.5$ ,  $[O_2]/[inert] = 0.27$

No.	Species	Formula	% C	Selectivity
1	Propenal		0.99	4.89
3	Propanal		3.51	17.39
17	Cyclohexene		0.99	4.90
20	Methylenecyclohexane		1.13	5.58
27	Cyclohexanone		1.02	5.07
33	Propyl-4-cyclohexene		3.00	14.85
36	Propyl-3-cyclohexene		0.98	4.86
45	Cyclohexanespiro-(ethyl-2-ox-2-irane)		1.08	5.34

The production of a lower aldehyde, a lower alkene, and OH after a C-C bond breaking arises for  $\beta$ - $^{\circ}QOOH$  radicals, which are of type  $^{\circ}Q_{i+2}(OOH)_i$  or  $^{\circ}Q_{i-2}(OOH)_i$ . The decomposition of a ketohydroperoxide produces a carbonylated radical, a carbonylated molecule, and OH; it is the low-temperature branching pathway.

Fig. 7 explains the formation of the major oxidation products of *n*-propylcyclohexane from the  $R_iO_2^{\circ}$  radicals:

- the origin of propenal is difficult to assess with certainty because of the numerous pathways that could be responsible for its formation.
- propanal can be formed by the radicals  $R_1O_2^{\circ}$  and  $R_3O_2^{\circ}$  resulting from the decomposition of a ketohydroperoxide.
- the  $\beta$ -scission of the propyl side chain of *n*-propylcyclohexane produces cyclohexene and propanal. Cyclohexene is formed by the radical  $^{\circ}Q_5(OOH)_3$  after a C-C bond breaking.
- methylenecyclohexane is formed after a C-C bond breaking as well as cyclohexene. In that case, the decomposition of the  $\beta$ - $^{\circ}QOOH$  radical  $^{\circ}Q_4(OOH)_2$  produces methylenecyclohexane and acetaldehyde, a light product which could not have been detected in our analyses.
- cyclohexanone is a ketone which can be formed from the radicals  $R_1O_2^{\circ}$ ,  $R_2O_2^{\circ}$  or  $R_3O_2^{\circ}$ . In each case, cyclohexanone is formed from the decomposition of a ketohydroperoxide.
- propyl-4-cyclohexene is a conjugate alkene produced from the radicals  $R_6O_2^{\circ}$  or  $R_7O_2^{\circ}$ . The

formation of this alkene is possible due to the formation of  $\alpha$ - $^{\circ}QOOH$  radicals which can undergo a C-O bond breaking.

- propyl-3-cyclohexene is another conjugate alkene, which is produced by the radicals  $R_5O_2^{\circ}$  or  $R_6O_2^{\circ}$ .
- cyclohexanespiro-(ethyl-2-ox-2-irane) is the only O-heterocycle identified in the main oxidation products. It is formed after a O-O bond scission followed by a cyclization from the radicals  $R_3O_2^{\circ}$  or  $R_4O_2^{\circ}$ .

## Conclusions

The autoignition of *n*-propylcyclohexane is studied in a rapid compression machine over the pressure range 4.5-13.4 bar, between 620 and 930 K, and for three equivalence ratios  $\phi$ : 0.3, 0.4, and 0.5. Overall, the ignition delay time of lean *n*-propylcyclohexane/ $O_2$ /inert mixtures increases when  $\phi$  is decreased from 0.5 to 0.3. The ignition limit strongly increases with the decrease of  $\phi$ . The ignition occurs in two stages for all  $\phi$  and  $P_0$ . At  $P_0 = 250$  torr a NTC zone is clearly visible for  $\phi = 0.5$  and 0.4. Concerning cool flame delay times, the equivalence ratio and the initial pressure seem to have no influence on the first stage of ignition. This can be explained this way : at low temperatures, the isomerization of  $R_iO_2^{\circ}$  into  $^{\circ}Q_j(OOH)_i$  radicals is the low-temperature branching limiting step, independently of the initial hydrocarbon concentration. The cool flame phenomenon will always be nearly independent of the equivalence ratio or the initial pressure. On the other hand, the autoignition depends on the formation of the radicals  $HO_2$  and  $H_2O_2$ , and depends also on the heat release

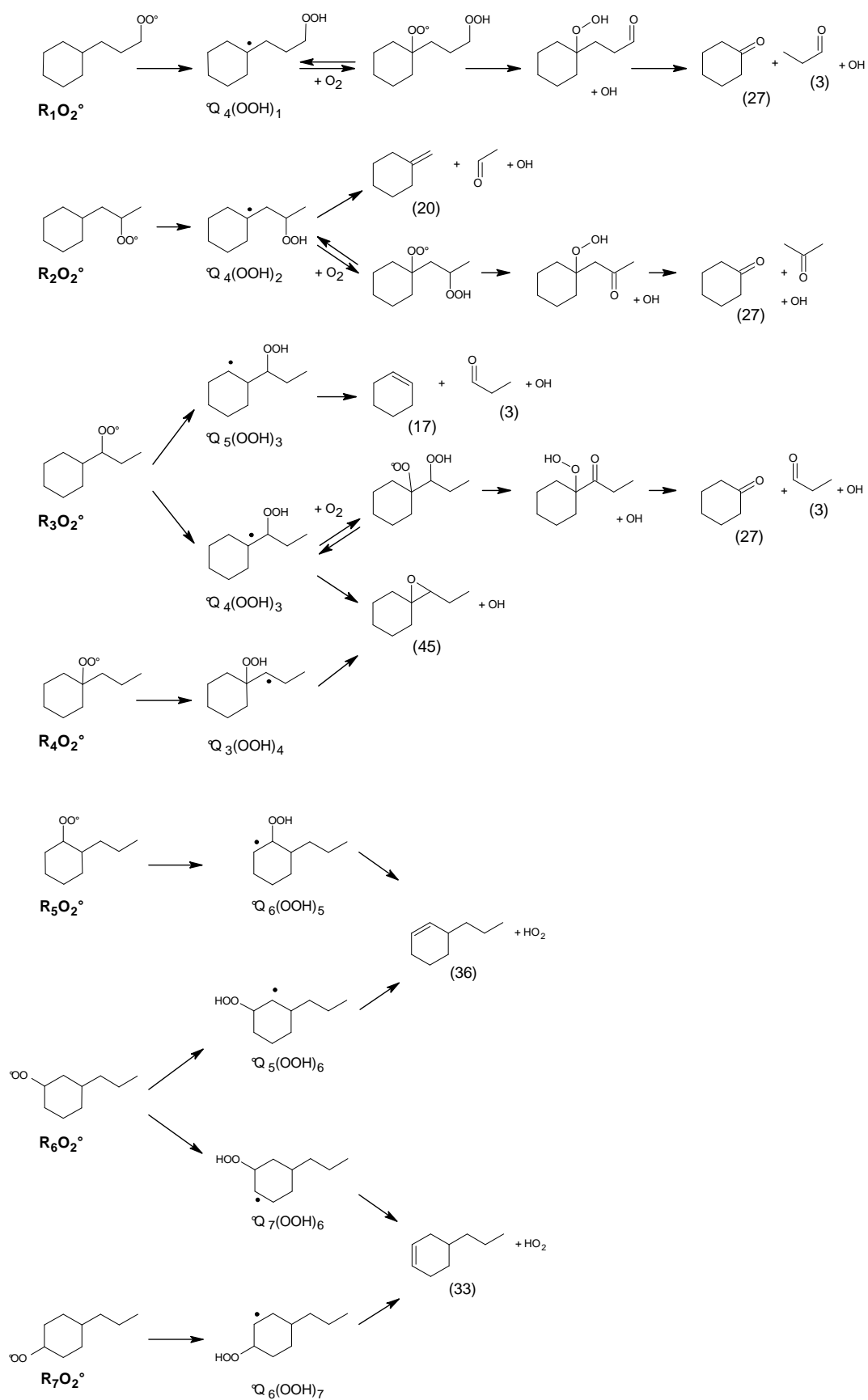


Fig. 7. Formation of the main oxidation products from the radicals  $R_1O_2^\bullet$  to  $R_7O_2^\bullet$ .

necessary to reach the temperature at which the reaction  $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2 \text{OH} + \text{M}$  occurs. The production of OH radicals is responsible for the autoignition phenomenon and is clearly dependent of  $\phi$  and  $P_0$ . Further investigations are needed to justify this explanation.

With the sample withdrawn from the combustion chamber, 47 oxidation products have been detected, among which the 8 major products have been quantified. Their plausible formation pathways at low-temperature have been suggested, with help of the low-temperature oxidation reaction scheme of alkanes. The identification and quantification of the other 39 products is still underway.

### Acknowledgements

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