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Theoretical Kinetic Study of the Reactions of Cycloalkylperoxy Radicals

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Reactions of alkyl radicals with oxygen are key reactions in the low-temperature oxidation of hydrocarbons, but they have not been extensively studied yet in the case of cycloalkanes. Isomerizations of cycloalkylperoxy radicals and formation of cyclic ethers are especially important. In the present work, a theoretical study of the gas-phase reactions of cyclopentylperoxy and cyclohexylperoxy radicals has been carried out by means of quantum chemical calculations at the CBS-QB3 level. Computations on cyclopentylperoxy decomposition pathways are reported here for the first time. Thermochemical data have been obtained by means of isodesmic reactions, and the contribution of hindered rotors has been explicitly taken into account. Transition state theory has been used to calculate rate constants for all the elementary reactions. Three-parameter Arrhenius expressions have been derived in the temperature range 300−1000 K. Tunneling effects have been accounted for in the case of H-atom transfers. Our results compare well with experimental data and previous calculations available in the literature. In particular, the predicted rate constants for processes involving cyclohexylperoxy radicals, which have been introduced in a reaction mechanism scheme proposed before, exhibit excellent agreement with experiments at low and intermediate temperatures.

Introduction

Reactions of alkyl radicals with oxygen are key reactions in atmospheric chemistry and in the low-temperature oxidation of hydrocarbons. The need for a precise simulation of the autoignition behavior of fuels is increasing with the development of new combustion modes, such as those occurring in homogeneous charge compression ignition engines. Indeed, the homogeneous charge in these engines makes autoignition an essentially chemically controlled process,[1] in contrast to conventional diesel and spark ignited engines. In the low-temperature range, the reaction of alkyl radicals with O_2 yields peroxy radicals ROO•, which typically isomerize to produce hydroperoxyalkyl radicals •QOOH. The latter can either decompose to yield cyclic ethers and •OH or react again with O_2 to produce ultimately hydroperoxides, which thanks to their fast decomposition into two free radicals are degenerate branching agents responsible for the autoignition of the mixture. The isomerization of peroxy radicals ROO• and the formation of cyclic ethers from •QOOH are important reaction steps for the understanding of hydrocarbons reactivity below the negative temperature coefficient.[2,3]

In recent years, many chemical kinetic studies have investigated the autoignition of linear and branched alkanes, but little attention has been paid to cyclic alkanes. However, naphtenes, and in particular those involving C_5 and C_6 rings, are present in significant amounts in conventional fuels (up to 3% in gasoline and up to 35% in diesel fuel).[4] Their chemistry is similar to that of alkanes, but the rate parameters of many reactions are affected by the ring structure. Unimolecular initiations of naphtenes lead to diradical species specific to the chemistry of cycloalkanes.[5] Cycloalkyl radicals produced by H-abstractions from cycloalkanes can decompose by C−C and C−H bond β-scission. While C−H bond breaking conserves the cyclic structure through the formation of the corresponding cycloalkene, C−C bond breaking occurs via a strained transition state and yields a linear unsaturated alkyl radical.[6] At low temperature, Pitz et al.[7] have shown the strong influence of isomerization rate parameters for cycloalkylperoxy radical reactions on ignition delay times in the negative temperature coefficient (NTC) region.

Few studies have been devoted to oxidation of cyclopentane. Besides, no data are available for the isomerization of cyclopentylperoxy radical nor for the decomposition of hydroperoxycyclopentyl radicals to cyclic ethers. Handford-Styring and Walker[8] found that cyclopentene was the major product in the oxidation of cyclopentane between 673 and 783 K, while acroleine and epoxycyclopentane were produced in smaller amounts. They concluded that cyclopentene is produced in a one-step reaction between cyclopentyl and O_2. Acroleine and 1,2-epoxycyclopentane would come from the decomposition of a hydroperoxycycloalkyl radical. In perfectly stirred reactor at 873 K, Simon et al.[9] could not observe any cyclic ethers; cyclopentene was mainly measured. These authors proposed the formation of cyclopentylperoxy radicals, which then isomerizes and decomposes to form cyclopentene and HO_2. More recently, DeSain and Taatjes[10] studied experimentally the formation of HO_2 radicals by the reaction of cyclopentyl and O_2 between 296 and 732 K. They concluded that HO_2 and cyclopentene would be produced directly from cyclopentylperoxy radicals.

Some recent studies have focused on the low-temperature oxidation of cyclohexane, since this molecule is the most common surrogate for naphtenes. The key role of both, the isomerization of peroxy radicals and the formation of cyclic ethers, has been highlighted, showing that rate parameters derived from linear alkanes reactions do not allow a correct simulation of the reactivity because the constrained transition states involve bicyclic structures.[7,11] The group of Walker[12,13]

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has investigated experimentally the oxidation of cyclohexane between 670 and 770 K in a closed vessel and has reported reaction rates for the isomerization of cyclohexylperoxy radicals. In a rapid compression machine and in the temperature range 600−900 K, Lemaire et al.[14] have observed cool flames and second-stage ignitions. Tanaka et al.[15] have obtained also a low-temperature behavior in a rapid compression machine in the case of the oxidation of methylcyclohexane and found that the ignition delay times were close to that of 2-heptene. The oxidation of cyclohexane has been investigated by Granata et al.[16] These authors have considered a simplified model that includes eight global reactions in the primary mechanism and used estimated rate parameters from linear and branched alkane data. Another model, proposed by Buda et al.,[11] has allowed both a correct simulation of ignition in a rapid compression machine[14] and a proper prediction of high-temperature results in a perfectly stirred reactor.[17,18] In that model, kinetic parameters from ref 12 have been used for the isomerizations of the peroxy radical, and energy barriers for the formation of bicyclic ethers have been calculated by quantum chemistry methods at the B3LYP/cbsb7 level of theory. Cavallotti et al.[19] have studied theoretically the isomerization of cyclohexylperoxy radicals and the formation of cyclic ethers. The geometry of the structures have been optimized at the B3LYP/6-31G(d,p) level and the energies determined with the G2(MP2) composite method. A more comprehensive study[20] of the reactions of cyclohexyl with O_2 has been proposed using calculations based on a modified G2(MP2) method and using master equation simulations. A mechanism has been derived and used to simulate the experimental measurements of OH and HO_2 production during cyclohexane oxidation, after adjusting some energy barriers. A model for the oxidation of methylcyclohexane in the low-temperature range has been developed by Pitz et al.[7] and validated against ignition delay times in a rapid compression machine. The influence of isomerization rate constants has been checked using different data sets: rate parameters were estimated by using structure−reactivity relationships based first on alkane reactions and then on cyclohexane reactions.[13] A good agreement with experimental delay times was obtained. These isomerization rate parameters have been used by Silke et al.[21] to model the oxidation of cyclohexane over a wide range of conditions.

In order to obtain the necessary data for modeling the low-temperature oxidation of cycloalkanes, rate parameters for the isomerization of peroxy radicals produced from cyclopentane and cyclohexane and the decomposition reaction of hydroperoxycycloalkyl radicals into bicyclic ethers have been evaluated in the present work by means of high-level quantum chemistry ab initio calculations. Geometries of reactants, products, and transition states have been fully optimized. The computed enthalpies of formation have been systematically compared with experimental values or with calculated energies using the THERGAS[22] software; this code is based on group additivity methods that are widely used when no experimental values are available. High-pressure-limit rate constants were calculated for all the reactions and comparisons were also performed with available kinetic data in the literature. Since experimental results in the low-temperature range are available in the case of cyclohexane, computed rate constants have been inserted into the mechanism of Buda et al.[11] to model ignition times in a rapid compression machine[14] and reaction in a perfectly stirred reactor.[17]

Calculation Methods

The energies of the reactants, transition states, and products have been calculated using the composite method CBS-QB3[23] and the calculations have been performed using Gaussian 03 Rev. C.02.[24] For the estimation of thermochemical and kinetic data, we have used the methodology described before for the reaction of cycloalkanes.[1,6] Main features are just summarized here. The geometry of all the species has been optimized at the B3LYP/cbsb7[25,26] level of calculation. The evaluation of the vibrational frequencies has been carried out at the same level and has allowed us to characterize energy minima (positive frequencies) and transition states (TS) (only one imaginary frequency). Intrinsic Reaction Coordinate (IRC) calculations have been systematically performed at the B3LYP/6-31G(d) level on TSs to verify the connected minima. Thermochemical data for species involved in this study have been computed at the composite CBS-QB3 level (enthalpies of formation, entropies, and heat capacities). Constrained torsions in cyclic structures have been treated as harmonic oscillators, while free alkyl groups have been treated as hindered rotors using the *hinderedRotor* option of Gaussian03.[27] Enthalpies of formation ($\Delta_f H°$) have been calculated using isodesmic reactions.

The rate constant for each elementary reaction has been calculated by assuming transition state theory (TST). Tunneling effects on C−H bond-breaking processes have been taken into account by using the transmission coefficient correction proposed by Wigner.[28] The activation enthalpy for each elementary reaction has been obtained from the expressions

$$\Delta H^{\ddagger}(R \rightarrow P) = (\Delta H^{\ddagger}_{1(\text{CBS-QB3})} + \Delta H^{\ddagger}_{-1(\text{CBS-QB3})} + \Delta_r H_{(\text{isodesmic})})/2$$

and

$$\Delta H^{\ddagger}(P \rightarrow R) = (\Delta H^{\ddagger}_{1(\text{CBS-QB3})} + \Delta H^{\ddagger}_{-1(\text{CBS-QB3})} - \Delta_r H_{(\text{isodesmic})})/2$$

where $\Delta H^{\ddagger}_{1(\text{CBS-QB3})}$ and $\Delta H^{\ddagger}_{-1(\text{CBS-QB3})}$ are the CBS-QB3 computed enthalpies of activation for the direct and reverse reactions, respectively, and $\Delta_r H_{(\text{isodesmic})}$ is the enthalpy of reaction estimated from isodesmic reactions.

In the text below, we shall often assimilate activation energy with activation enthalpy calculated from TST; this quantity includes electronic energy, ZPE, and thermal corrections due to translational, vibrational, and rotational degrees of freedom. In the case of unimolecular reactions involved here, $\Delta^{\ddagger}H°$ differs from classical Arrhenius activation energy by the quantity RT.

Kinetic data are obtained by fitting the computed TST rate constants at several temperatures (300−1000 K) with a modified Arrhenius equation

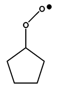
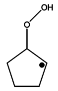
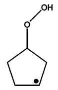
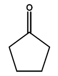
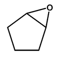
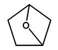
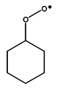
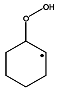
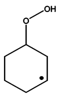
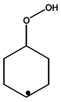
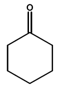
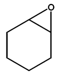
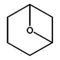
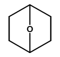
$$k_{\infty} = AT^n \exp(-E/RT)$$

where A, n, and E are parameters and k_{∞} is the high-pressure limit. It must be kept in mind that the fit parameter E is different from the calculated TST activation energy E_a at any temperature.

Thermochemical Data

Thermochemical data ($\Delta_f H°$, $S°$, $C_p°$) for all species are summarized in Table 1. The calculated enthalpies of formation for cyclic ketones and 1,2-epoxides are in good agreement with experimental ones.[29] No data was available for the other cyclic ethers. For free radicals, our values are close to those estimated using additivity methods,[22] though they show an average

TABLE 1: Ideal Gas Phase Thermodynamic Properties Obtained by CBS-QB3 Calculations and Isodesmic Reactions[b]

			$C^\circ_p(T)$							$\Delta_f H^\circ_{298K}$
Species	$\Delta_f H^\circ_{298K}$	$S^\circ_{298\,K}$	300 K	400 K	500 K	600 K	800 K	1000 K	1500K	*Literature*
	-11.7	84.6	27.6	36.2	43.8	50.1	59.7	66.5	76.7	*-8.0*
	4.3	86.4	30.7	39.0	46.1	52.0	60.7	66.9	76.3	*3.5*
	3.7	86.6	30.6	39.0	46.2	52.1	60.9	67.2	76.6	*-0.7*
	-47.5	75.2	23.1	30.7	37.5	43.2	51.8	57.9	67.1	-47.2
	-22.9	71.8	21.7	29.9	37.0	42.9	51.7	57.9	67.1	-23.2
	-13.4	70.0	20.8	29.4	36.9	42.9	51.8	58.0	67.1	-
	-22.3	87.7	32.0	42.3	51.4	59.1	70.8	79.1	91.6	*-19.6*
	-4.4	91.1	34.8	44.7	53.4	60.7	71.8	79.7	91.7	*-8.1*
	-4.5	91.7	35.2	45.1	53.7	60.9	71.8	79.6	91.3	*-7.3*
	-4.6	91.3	35.2	45.0	53.7	60.9	71.8	79.6	91.3	*-7.3*
	-55.7	80.1	27.4	36.7	45.0	52.0	62.7	70.4	82.0	-55.2
	-30.3	77.2	26.3	35.9	44.6	51.8	62.7	70.5	82.0	-30.0
	-25.6	75.7	25.4	35.5	44.4	51.7	62.7	70.5	82.0	-
	-43.8	74.9	24.9	35.2	44.2	51.7	62.7	70.4	81.9	-42.4[a]

[a] From ref 11. [b] Enthalpy is expressed in kcal mol^{-1}, and entropy and heat capacity are given in cal mol^{-1} K^{-1}. The last row gives either the experimental value of $\Delta_f H^\circ_{298K}$ cited in NIST database[29] or the estimation made using group additivity methods[22] (in italic).

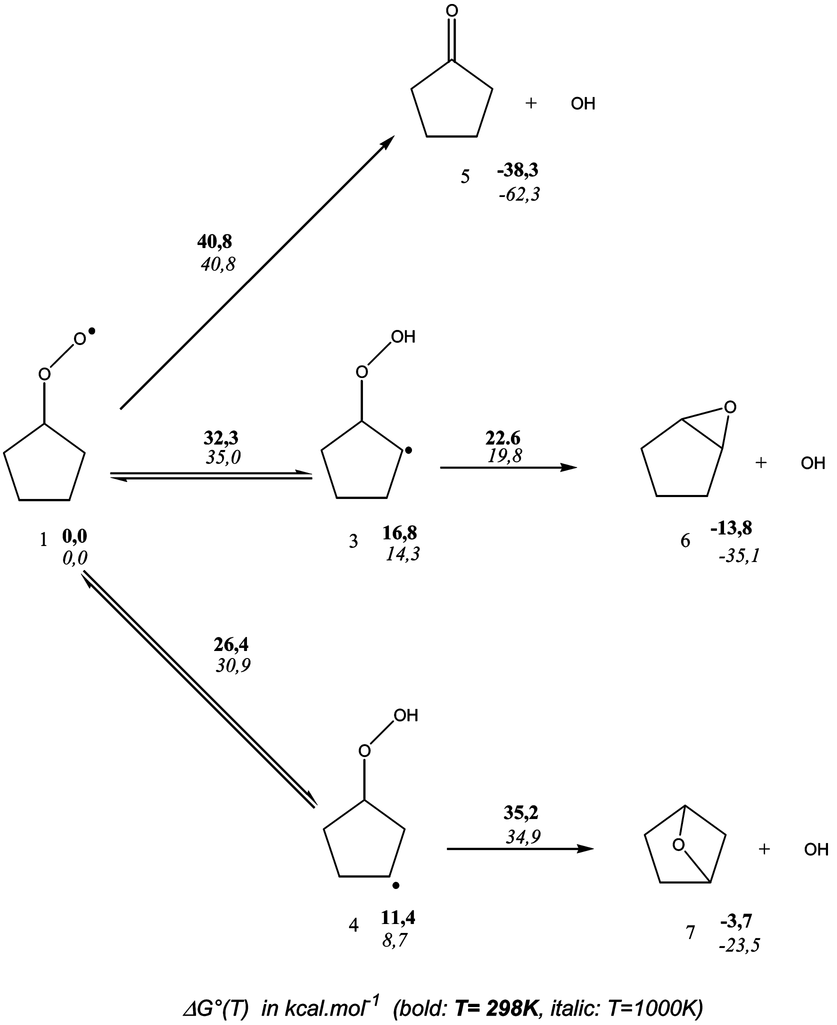
discrepancy of 3−4 kcal mol^{-1}. This difference might be due to the calculation method used by the THERGAS program to evaluate radical enthalpies of formation using tabulated bond dissociation energies (BDE). The energy of the radical is evaluated from a model molecule. The reference BDE is an average value from the literature for a similar bond but may be not very accurate for the cyclic free radicals. Note that this discrepancy can lead to large changes in the calculated equilibrium constant for the oxygen addition reaction and, therefore, in the value of the rate constant for the reverse reaction.

Reactions of Cyclopentylperoxy Radicals

The isomerization of cyclopentylperoxy radicals and the decomposition to bicyclic ethers of the hydroperoxycyclopentyl radicals are presented in Scheme 1. In all the schemes presented hereafter, Gibbs energies are reported in kcal mol^{-1} at 298 K (bold) and 1000 K (italic), and are relative to the reference peroxycycloalkyl radical.

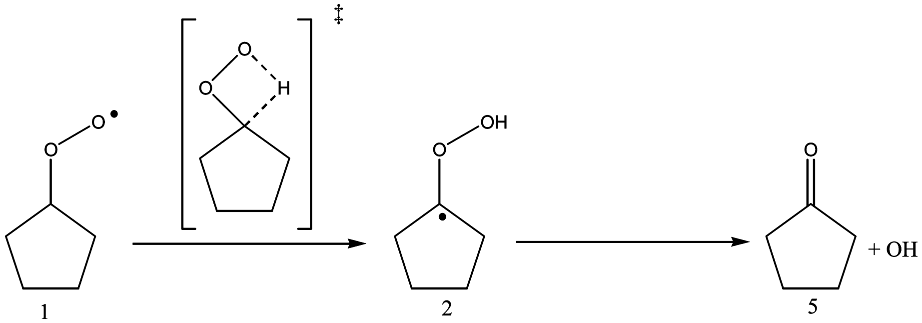
The cyclopentylperoxy radical can isomerize through three different pathways all involving bicyclic transition states (TS).

SCHEME 1: Isomerizations of Cyclopentylperoxy Radicals and Decomposition of Hydroperoxycyclopentyl Radicals to Cyclic Ethers[a]



[a] Free energies are relative to the cyclopentylperoxy radical **1**.

SCHEME 2: Isomerization of the Cyclopentylperoxy Radical to 1-Hydroperoxycyclopentyl Radical and Decomposition to Cyclopentanone

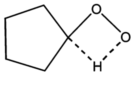
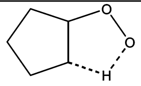
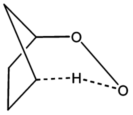


In the first one (top process in Scheme 1), there is a transfer of the H-atom in the tertiary carbon atom to the terminal oxygen of **1**, via a bicyclic TS composed of four- and five-atom rings (Scheme 2). The IRC calculation from this TS showed that it directly leads to cyclopentanone **5** and hydroxyl radical, the hydroperoxycyclopentyl intermediate radical **2** (see Scheme 2) being unstable at the B3LYP/cbsb7 level. Indeed, geometry optimization of this intermediate systematically leads to dissociation into cyclopentanone and hydroxyl radical, illustrating the weakness of an O−O bond in the beta position of a radical center. A direct reaction from **1** to **5** has then be assumed; it involves an activation energy of 40.6 kcal mol^{-1}.

The second isomerization (central process in Scheme 1) yields 2-hydroperoxycyclopentyl radical **3** through a bicyclic TS composed of two five-atom rings. The corresponding activation energy is 31.1 kcal mol^{-1} at 298 K, which is 9.5 kcal mol^{-1} lower than the activation energy for the **1** → **5** isomerization above.

The third isomerization reaction (bottom process in Scheme 1) produces the 3-hydroperoxycyclopentyl radical **4** via a

TABLE 2: Comparison between Activation Energies from Ab Initio Calculations ($E_a^{\text{CBS-QB3}}$) and the Semiempirical Method Described in the Text ($E_a^{\text{semiempirical}}$) for the Isomerization of Cyclopentylperoxy Radicals[e]

Structure of the TS	E_{abs} [11]	RSE of model bicyclic hydrocarbon	ΔE_{RSE}	$E_a^{\text{semi-empirical}}$	$E_a^{\text{CBS-QB3}}$
 **TS(1→5)**	12	-	23[c]	35	40.6
 **TS(1→3)**	17	16.5[a]	16.5 – 7.1[d] = 9.4	26.4	31.1
 **TS(1→4)**	17	10.6[b]	10.6 – 7.1[d] = 3.5	20.5	24.4

[a] From ref 30 [b] Calculated at the CBS-QB3 level from isodesmic reactions. [c] In the case of two rings connected by a single atom, the influence of the five-membered ring has been neglected and ΔE_{RSE} is taken as equal to that of acyclic alkanes.[11] [d] The RSE of cyclopentylperoxy radical is taken equal to that of cyclopentane, i.e., 7.1 kcal mol^{-1}.[30] [e] ΔE_{RSE} is the difference in RSE between the TS and the reactant. Values are in kcal mol^{-1}.

bicyclic TS displaying five- and seven-membered rings. This last route appears to be the most favorable one, the activation energy being 24.4 kcal mol^{-1}. The formed radical **4** is more stable than **3** by 5.4 kcal mol^{-1} (free energy at 298 K).

A widely used semiempirical method for evaluating the activation energy of this type of isomerization processes lies on the separation of two energy contributions: the barrier for the internal H-abstraction and the so-called ring strain energy (RSE). Accordingly, the activation energy is written as

$$E_a = E_{abs} + \Delta E_{RSE} \tag{1}$$

In our case, E_{abs} represents the activation energy for H-abstraction by a peroxy radical ROO• and ΔE_{RSE} the difference in RSE between the cyclopentylperoxy radical and the bicyclic TS. It is interesting to compare our calculations for activation energies with values obtained using this method. E_{abs} values have been proposed by Buda et al.,[11] but no data are available for the RSE of bicycles containing two O-atoms. Roughly, RSE for TSs can be estimated from the corresponding hydrocarbon bicycle, when available, or from the reaction of acyclic alkanes. Table 2 compares the activation energies calculated at the CBS-QB3 level with those estimated from the semiempirical method.

The semiempirical approach underestimates the activation energies strongly, showing differences with respect to CBS-QB3 calculations of 4.7, 5.6, and 3.9 kcal mol^{-1}, for reactions **1** → **5**, **1** → **3**, and **1** → **4**, respectively. At 750 K, the semiempirical rate constants would be, respectively, 43, 23, and 14 times greater than the ab initio ones. This fact can be explained by large errors introduced in the estimation of RSE from hydrocarbons, which is probably an unsuitable approximation for TSs that actually include peroxy groups. Thus, the lack of data for bicyclic systems makes theoretical calculations necessary.

The stable hydroperoxycyclopentyl radicals **3** and **4** can decompose into cyclic ethers, 1,2-epoxycyclopentane (**6**) and 1,3-epoxycyclopentane (**7**), respectively (see Scheme 1). The reaction **3** → **6** is much easier since the corresponding activation energy (10 kcal mol^{-1} at 298 K) is substantially lower than that required by the **4** → **7** reaction (23.0 kcal mol^{-1} at 298 K). Moreover, the **3** → **6** activation energy is lower than in similar processes for linear alkanes. Thus, according to Baldwin et al.,[31] the formation of 1,2-epoxide from hydroperoxypropyl radical requires an activation energy of 16.5 kcal mol^{-1}. For heavier alkanes, Buda et al.[32] have reported an activation energy of 17.95 kcal mol^{-1}, whereas Curran et al.[33] have reported a higher value, 22.0 kcal mol^{-1}. From CBS-QB3 calculations, Wijaya et al.[34] have calculated activation energies values between 13.4 and 17.0 kcal mol^{-1} in the case of the decomposition of various β-hydroperoxyalkyl radicals to oxirane. The authors found that the presence of alkyl groups connected to the carbon bearing the radical center lowers the energy barrier because of release of strain energy in the transition state.

In contrast to this reaction, the **4** → **7** reaction yielding 1,3-epoxycyclopentane has a higher activation energy (23.0 kcal mol^{-1}) than that involved in linear alkanes to produce an oxetane. For oxetane formation in the case of alkanes, the studies cited above have reported activation energies of 15.5 kcal mol^{-1},[31] 16.6 kcal mol^{-1},[32] 15.25 kcal mol^{-1},[33] whereas estimations from theoretical calculations vary in the range 17.4−21.9 kcal mol^{-1}.[34]

The high activation energy predicted here for the formation of 1,3-epoxycyclopentane may be attributed to significant bond angle deformations in reaching the TS. The change is expected to dramatically affect the sp^3 structure of the C-atoms and to cause a strong molecular strain increase. This effect is illustrated by the difference in energy of the epoxycyclopentanes **6** and **7**. The free enthalpy of the latter is 10.1 kcal mol^{-1} higher than that of 1,2-epoxycyclopentane due to the change of the RSE.

TABLE 3: Kinetic Parameters for the Isomerization of Cyclopentylperoxy Radicals and Decomposition of Hydroperoxycyclopentyl Radicals to Cyclic Ethers[a]

	A (s^{-1})	n	E (kcal mol^{-1})
$k(\mathbf{1}\rightarrow\mathbf{5})$	9.55×10^{8}	1.370	40.24
$k(\mathbf{1}\rightarrow\mathbf{3})$	1.41×10^{7}	1.767	28.16
$k(\mathbf{1}\rightarrow\mathbf{4})$	6.31×10^{6}	1.712	24.34
$k(\mathbf{3}\rightarrow\mathbf{6})$	1.62×10^{10}	0.997	7.27
$k(\mathbf{4}\rightarrow\mathbf{7})$	1.48×10^{10}	0.802	22.79

[a] From fitted rate constants at $300 \text{ K} \le T \le 1000$ K.

To summarize this part, we can say that the most favorable reaction route for cyclopentylperoxy radicals is isomerization to **3**, followed by decomposition to 1,2-epoxycyclopentane **6**. In this pathway, the limiting step is the first one, i.e. isomerization, involving a free energy barrier of 32.3 kcal mol^{-1} at 298 K. Kinetic parameters for processes in Scheme 1 have been calculated between 300 and 1000 K and are summarized in Table 3. No kinetic data is available in the literature for these reactions. Note, however, that Hanford-Styring and Walker[8] have detected only 1,2-epoxycyclopentane as a cyclic ether during the oxidation of cyclopentane, what is consistent with our conclusions.

Reactions of Cyclohexylperoxy Radical

Scheme 3 displays the isomerization reactions for the cyclohexylperoxy radical and the decomposition into bicyclic ethers of the hydroperoxycyclohexyl radicals. As before, Gibbs free energies are reported in kcal mol^{-1} at 298 K (bold) and at 1000 K (italic) and are relative to the reference peroxycyclohexyl radical.

Four isomerization channels are possible here. The first one consists in transferring the H atom in the tertiary C atom through a TS involving a four-membered ring, as illustrated in Scheme 4. As for the cyclopentylperoxy radical described above (Scheme 2), this reaction leads to an unstable hydroperoxyalkyl radical, which spontaneously decomposes to cyclohexanone and OH. This has been verified by IRC calculations at the B3LYP/cbsb7 level. The activation energy is 39.2 kcal mol^{-1}. It is close to that obtained for the cyclopentylperoxy reaction (40.6 kcal mol^{-1}), and therefore, this decomposition mechanism seems not very sensitive to the size of the initial cycloalkane.

In the second isomerization process, an H-atom is transferred through a TS involving a five-membered ring leading to the hydroperoxycyclohexyl radical **3**. The energy barrier, 31.6 kcal mol^{-1}, is lower than that involved in the first route but is close to that of the corresponding reaction of cyclopentylperoxy radicals (31.1 kcal mol^{-1}). In the case of bicyclic transition states where the two cycles are connected by an atom or a single bond, the size of the ring involved in the reactant seems to have little influence on the energy barrier.

The third isomerization involves a 1,5-atom transfer and therefore a TS with a six-membered ring, yielding the hydroperoxycyclohexyl radical **4**. This isomerization is the easiest one, with an activation energy of 25.1 kcal mol^{-1}, close to the equivalent one in the cyclopentylperoxy radical case (24.4 kcal mol^{-1}). Finally, the isomerization yielding the hydroperoxycyclohexyl radical **5** involves a 1,6-atom transfer and a seven-membered ring TS. The corresponding activation energy is 30.3 kcal mol^{-1} (comparison cannot be made with the cyclopentylperoxy radical in this case, since no equivalent process is possible for the latter).

In Table 4, we compare our computed activation energies and the values proposed by Buda et al.[11] based on semiempirical calculations, as described before.

Our predicted activation energies differ considerably from semiempirical ones, showing an absolute deviation between 4.2 and 7.7 kcal mol^{-1}. Semiempirical estimations underestimate activation energies of reactions $\mathbf{1} \rightarrow \mathbf{5}$ and $\mathbf{1} \rightarrow \mathbf{6}$ and overestimate those of reactions $\mathbf{1} \rightarrow \mathbf{3}$ and $\mathbf{1} \rightarrow \mathbf{4}$. This comparison confirms the strong limitation of the usual semiempirical methods in the case of cyclic reactants, especially when reactions involve a bicyclic transition state.

Hydroperoxyhexyl radicals decompose mainly to cyclic ethers. As shown in Scheme 3, the most favorable reaction is that forming 1,2-epoxycyclohexane ($\mathbf{3} \rightarrow \mathbf{7}$), while the formation of 1,3-epoxycyclohexane ($\mathbf{4} \rightarrow \mathbf{8}$) is the most difficult one. Note that 1,4-epoxycyclohexane (**9**) is much more stable than the other two cyclic ethers (**7** and **8**). This is consistent with the experimental observation[8] that 1,3-epoxycyclohexane decomposes very easily in a molecular reaction to hex-5-en-1-al.

It is interesting to remark that the formation of 1,2-epoxide from hydroperoxycyclopentyl and hydroperoxycyclohexyl involves similar activation energy, 10.1 and 10.0 kcal mol^{-1}, respectively, whereas the formation of 1,3-epoxide requires more energy in the latter case (23.0 kcal mol^{-1} vs 19.0 kcal mol^{-1}).

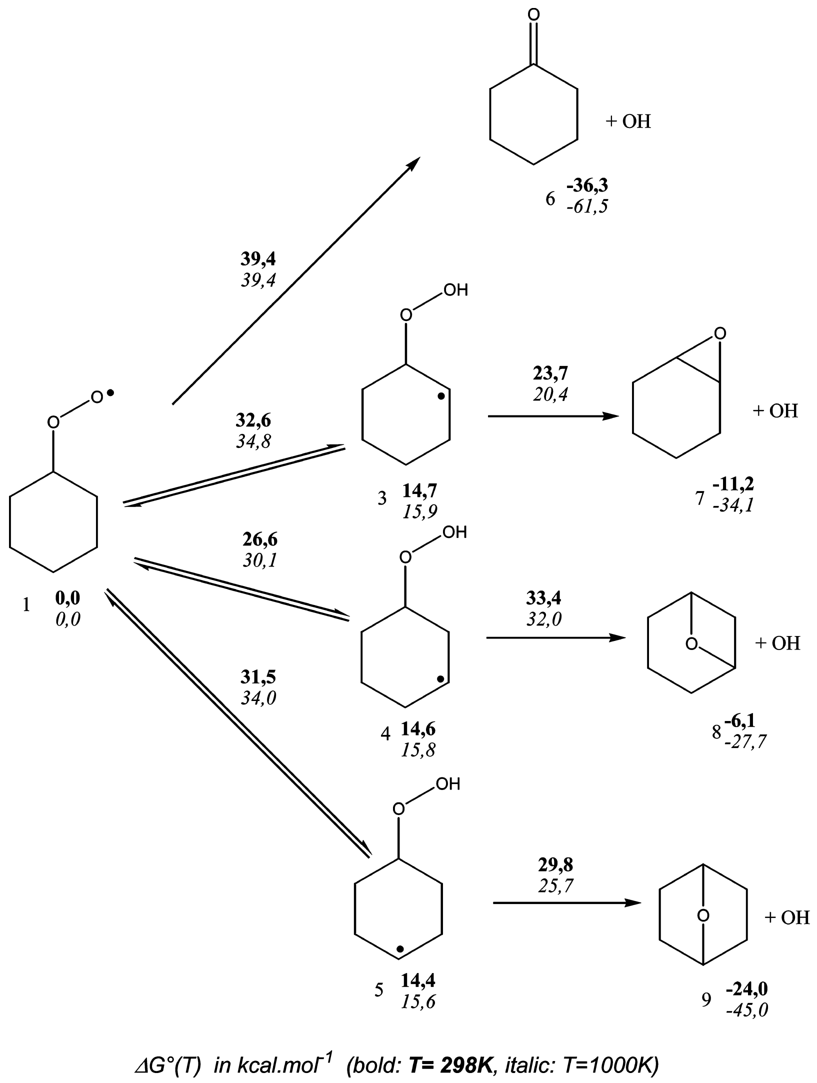
Kinetic parameters of the isomerizations and decompositions to cyclic ethers presented in Scheme 3 have been derived from the calculations between 300 and 1000 K and are summarized in Table 5. They are discussed below.

Comparison to Literature Data

Calculated rate parameters are now compared to literature data for cyclohexylperoxy radical. Walker and co-workers[8,12] derived isomerization rates from fitting their experimental results by a complex mechanism. Buda et al.[11] and Pitz et al.[7] estimated rate parameters by semiempirical methods modified to reproduce experimental data. Specifically, Pitz et al. modified their semiempirical data determined for linear alkanes in order to reproduce ratios between isomerization reactions proposed by Walker.[12,13] Cavalotti et al.[19] performed quantum chemistry calculations with a modified G2MP2 method. The authors optimized geometries using DFT at the B3LYP/6-31G(d,p) level (instead of the usual MP2/6-31G(d,p)) level and applied the G2MP2 composite method afterward. The tunneling effect was not taken into account. Figure 1 compares rate constants calculated in the present work with values from references cited above.

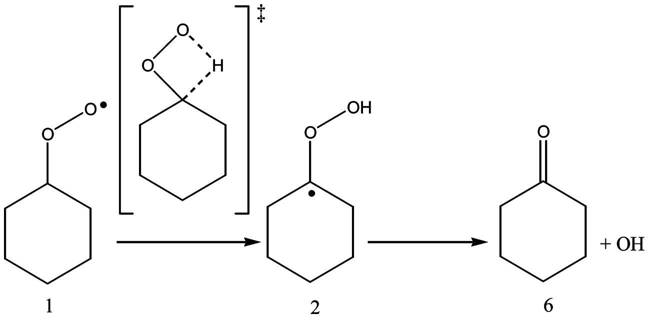
Let us first consider the case of the 1,4 atom shift (reaction $\mathbf{1} \rightarrow \mathbf{3}$, Figure 1a). Our rate constant is slightly higher than the other estimations in the full temperature range. Data from Pitz et al.[7] is always quite below all the other values. At 750 K, our rate constant is greater than that of Cavalotti et al.,[19] Buda et al.,[11] and Handford-Styring and Walker[13] by a factor 2, 1.4, and 1.8, respectively, which can be considered as a reasonably good agreement. In contrast, a factor of 8 was found with respect to Pitz et al. It must be noted that the tunneling effect (estimated here from Wigner's approximation) leads to a non-negligible increase of the rate constant, amounting a factor of 1.7 at 750 K. In the case of the 1,5 atom shift (reaction $\mathbf{1} \rightarrow \mathbf{4}$, Figure 1b), the value of Cavalotti et al. is greater than ours by a factor 1.7 at 750 K, while our rate constant is greater than those of Pitz at al., Buda et al., and Handford-Styring and Walker, by 28, 6.8, and 8.8, respectively, at the same temperature. Finally, for the 1,6 atom shift (reaction $\mathbf{1} \rightarrow \mathbf{5}$, Figure 1c), our rate constant is in very good agreement with all other estimations except with that of Pitz et al. (factors between 1.4 and 1.7 at 750 K with respect to estimations other than that of Pitz et al. and a factor of 11 with respect to the value of Pitz et al. at the same temperature).

SCHEME 3: Isomerizations of the Cyclohexylperoxy Radical and Decomposition into Cyclic Ethers of the Hydroperoxycyclohexyl Radicals[a]



[a] Energies are relative to the cyclohexylperoxy radical **1**.

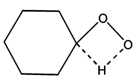
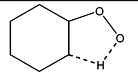
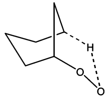
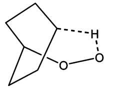
SCHEME 4: Isomerization of the Cyclohexylperoxy Radical to 1-Hydroperoxycyclohexyl Radical and Decomposition to Cyclohexanone



Kinetic parameters for the decomposition of hydroperoxycyclohexyl radicals to cyclic ethers are now compared to calculations proposed by Buda et al.[11] and Cavallotti et al.[19] Buda et al. determined the energy barriers by DFT at the B3LYP/cbsb7 level and estimated the pre-exponential factor by using a semiempirical approach. Cavallotti et al. calculated the rate constants with the modified G2MP method. Data reported by Pitz et al.,[7] corresponding to slightly modified values of Cavallotti et al., are not discussed here. Figure 2 displays the comparison.

A rather good agreement for the three reactions is observed between our calculations and those of Buda et al., [11] which is not surprising considering that geometries and vibrational analyses have been performed at the same level of theory. At 750 K, our rate constants and those of Buda et al. exhibit a ratio of 1.5, 4, and 1.6, for reactions **3** → **7**, **4** → **8**, and **5** → **9**, respectively (Figure 2). In contrast, values calculated by Cavallotti et al. are dramatically lower. At 750 K, our rate constants are greater by a factor of 37, 880, and 42 for reactions **3** → **7**, **4** → **8**, and **5** → **9**, respectively. This strong discrepancy comes from both pre-exponential factor and activation energy. Our activation energies are, respectively, 4.4, 4.1, and 4 kcal mol^{-1} lower than those reported by Cavallotti et al. for the three reactions (i.e., 10.1, 19.0, and 16.7 kcal mol^{-1} in our work against 15.4, 23.4, and 20.7 kcal mol^{-1}). Knepp et al.,[20] using the same modified G2(MP2) method, calculated energy barriers values of 13.5, 22.7, and 20.7 kcal mol^{-1}, respectively. They used their data to simulate OH and HO_2 amounts formed during a Cl-initiated oxidation of cyclohexane. Interestingly, in order to obtain a "much better agreement with the HO_2 production",

TABLE 4: Comparison between Theoretical ($E_a^{\text{CBS-QB3}}$) and Semiempirical ($E_a^{\text{semiempirical}}$) Activation Energies (see eq 1) for Isomerizations of the Cyclohexylperoxy Radical[a]

TS Structure	E_{abs}	ΔE_{RSE}	$E_a^{\text{semi-empirical}}$	$E_a^{\text{CBS-QB3}}$
 **TS(1→6)**	12	23	35	39.2
 **TS(1→3)**	17	18.3	35.3	31.6
 **TS(1→4)**	17	15.8	32.8	25.1
 **TS(1→5)**	17	7.5	25.5	29.3

[a] Parameters used to determine $E_a^{\text{semiempirical}}$ are taken from Buda et al.[11] The ring strain energy of cyclohexane is considered to be 0 kcal mol^{-1}. Values are in kcal mol^{-1}.

TABLE 5: Kinetic Parameters of the Isomerizations of Cyclohexylperoxy Radicals and Decomposition of Hydroperoxycyclopentyl Radicals to Cyclic Ethers (300 K ≤ *T* ≤ 1000 K)

	log *A* (s^{-1})	*n*	*E* (kcal mol^{-1})
k(**1**→**6**+OH)	1.05×10^9	1.355	38.85
k(**1**→**3**)	3.63×10^8	1.401	31.74
k(**1**→**4**)	1.82×10^7	1.668	25.10
k(**1**→**5**)	1.05×10^7	1.739	30.25
k(**3**→**7**+OH)	4.90×10^{11}	0.564	10.25
k(**4**→**8**+OH)	3.31×10^{13}	0.248	20.44
k(**5**→**9**+OH)	4.17×10^{10}	0.935	16.40

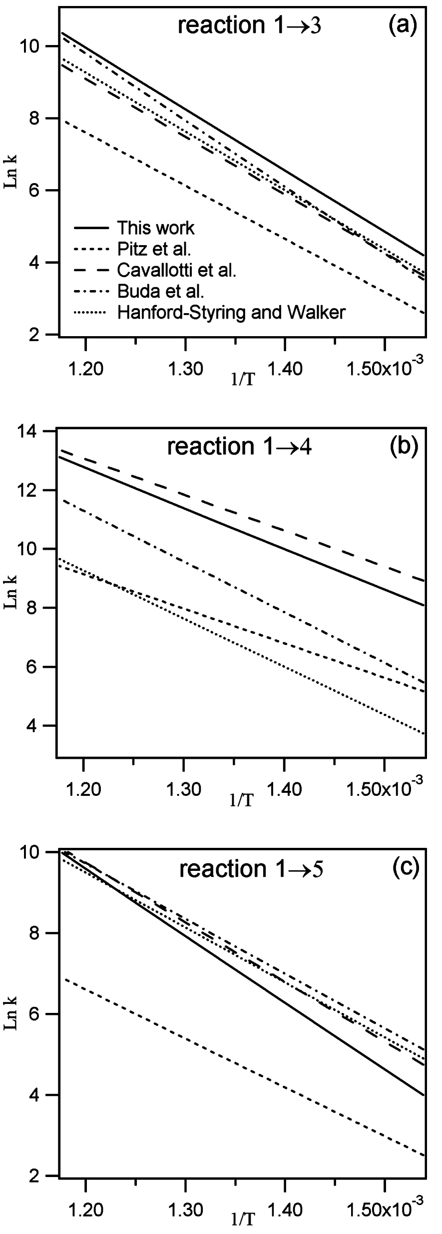


Figure 1. Comparison between rate constants for isomerization of cyclohexylperoxy radical calculated in this work and other values proposed in the literature.[7,11,13,19] (650 K < *T* < 850 K).

the energy barriers of the cyclic ether formation were lowered to 11.5, 18.3, and 19.7 kcal mol^{-1}, respectively. These values are quite closer to ours, especially the second one, which concerns the most sensitive reaction among the three pathways.

Determining the origin of such a noticeable divergence will require further investigations, since the G2MP2 and CBS-QB3 theoretical methods are expected to provide close results. Indeed, as shown above, a rather good agreement is obtained for the cyclohexylperoxy radical isomerizations. This suggests that a possible explanation could come from spin-contamination consideration. While spin contamination is of minor importance in the case of isomerization processes ($\langle \hat{S}^2 \rangle$ around 0.8 in TSs), it is much larger in the processes leading to formation of cyclic ethers ($\langle \hat{S}^2 \rangle = 1.2$ in one case). Energies of spin-contaminated species can be doubtful. While the modified G2MP2 method employed by Cavallotti et al. does not contain any spin-contamination correction to total energy, the CBS-QB3 method does. Matheu et al.[35] reported spin-contaminated transition states in their study of cyclic alkyl radical reactions at the CBS-Q level of calculation and concluded that the spin contamination correction was sufficient on the basis of comparison with DFT calculations.

Low-Temperature Oxidation of Cyclohexane

In order to test the rate parameters computed in this work, the low-temperature oxidation of cyclohexane has been simulated. Due to the lack of experimental data for cyclopentane oxidation, no simulation has been performed in that case. Our aim is to check whether our rate parameters offer an opportunity to improve existing reaction models rather than to develop new models. The starting point is therefore the mechanism proposed by Buda et al.[11] Thermochemical properties and rate parameters have been redefined in the following way:

Rate constants for the unimolecular initiation reaction leading to 1-hexene via a diradical pathway are taken from ref 5.

Rate constants for cyclohexyl radical decompositions through C−C or C−H bond breaking are taken from ref 6.

Parameters for the isomerization−decomposition reactions of hydroperoxycyclohexyl radicals to yield cyclic ethers come from the present work. Note that 1,3-epoxycyclohexane, appearing in the decomposition of the 3-hydroperoxycyclohexyl radical in the Buda et al. mechanism, was replaced here by hex-5-en-1-al. As experimentally observed by Handford-

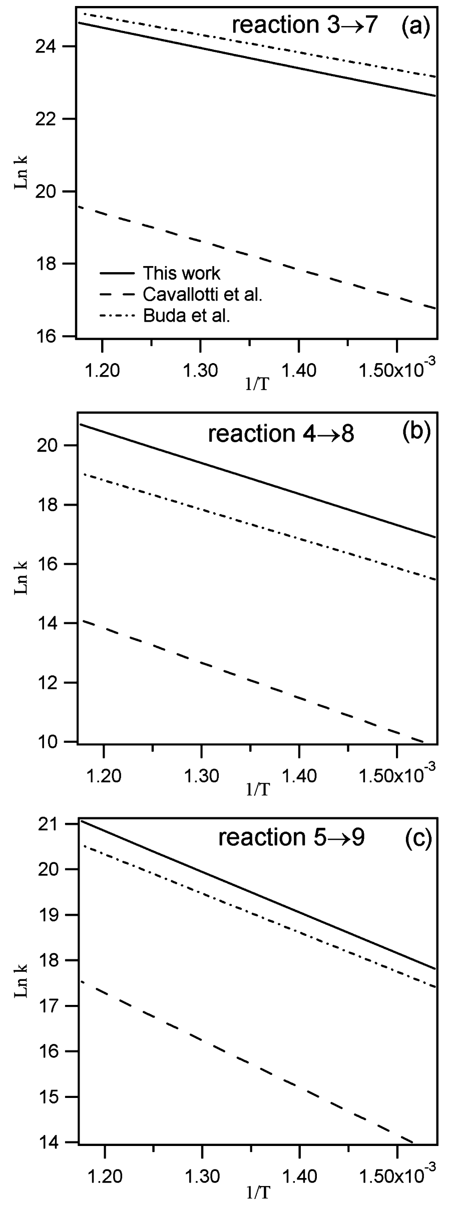


Figure 2. Comparison between rate constants of decomposition to cyclic ethers of hydroperoxycyclohexyl radicals calculated in this work and those proposed in the literature.[7,11] (650 K < T < 850 K).

Styring and Walker,[8] a very fast four-center pericyclic reaction produces the aldehyde from the cyclic ether (Scheme 5).

Rate parameters for decomposition of hydroperoxycyclohexyl radicals by β-scission have been estimated by analogy with cyclohexyl radicals by neglecting the influence of the hydroperoxy group.

In the same way, isomerization rate parameters for hydroperoxycyclohexylperoxy radicals •OOQ(OOH) were assumed to be equivalent to those calculated in this work for hydroperoxycyclohexyl radicals. However, when the internal atom-shift in •OOQ(OOH) involves the H-atom bonded to the tertiary C-atom (the one bearing the −OOH group), the activation energy is decreased by 5 kcal mol^{-1}. This correction is made to account for C−H bond weakening and has been determined in the modeling of alkane oxidation.[32] Internal H-abstraction of a tertiary H-atom by a peroxy radical involves an energy barrier 3 kcal mol^{-1} lower than that for abstracting a secondary H-atom. The presence of the O-atom in the α-position of the abstracted H-atom further decreases the barrier by around 2 kcal mol^{-1}.

For the O_2 addition to cyclohexyl radicals, Buda et al.[11] proposed a rate constant 3 times smaller than that used for the corresponding reaction with alkyl radicals.[32] This modification was necessary to improve their model in the low-temperature range and was justified by uncertainties on rate constants and changes in molecular structure. However, since mechanisms for aliphatic and branched alkanes have been widely validated,[32] we have preferred to use here the rate constant for O_2 addition to secondary alkyl radicals, without further adjustment, i.e. a value $6 \times 10^{+18}\ T^{-2.5}$.

Thermochemical properties of cyclohexyl, cyclohexylperoxy, and hydroxycyclohexyl have been taken from a previous study on cycloalkyl radicals decomposition[6] and from calculations in the present work.

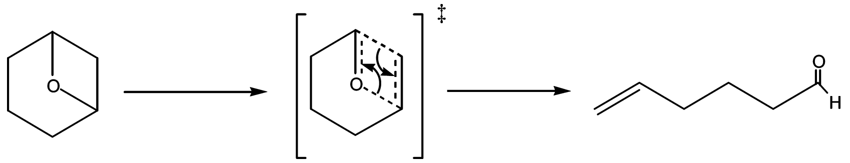
In order to reproduce the reactivity of benzene, which is among the major reaction products, a submechanism for benzene oxidation developed by some of us[36] has been added to the model. This submechanism contains 135 reactions involving benzene, a series of radicals (cyclohexadienyl, phenyl, phenylperoxy, phenoxy, hydroxyphenoxy, cyclopentadienyl, cyclopentadienoxy and hydroxycyclopentadienyl), as well as *o*-benzoquinone, phenol, cyclopentadiene, cyclopentadienone, and vinylketene, which are the primary products yielded. Model validations were made against experimental profiles obtained in a jet-stirred reactor, a plug flow reactor, in a laminar flame, and with shock tube autoignition delay times.[36]

Simulations have been performed using SENKIN and PSR of CHEMKIN II.[37] Lemaire et al.[14] studied the oxidation and the autoignition of cyclohexane in a rapid-compression machine between 600 and 900 K and pressures from 7 to 16.3 bar. The total autoignition delay times were measured between the end of compression and the rise of pressure due to the final ignition, whereas the cool flame delay times were characterized by the maximum intensity of the associated light emission. Figure 3 displays a comparison between computed and experimental cool flame and ignition delay times as a function of temperature for stoichiometric mixtures and for an initial pressure before compression of 350 Torr (Figure 3a), 550 Torr (3b), and 600 Torr (3c).

As shown, the model fits well the experimental results, except for a slight overprediction of the reactivity in the lowest temperature range, below 700 K. The position and the amplitude of the negative temperature coefficient (NTC) is well-reproduced. Selectivities are also well-predicted in the case of typical low-temperature products. The major intermediate product is hex-5-en-1-al, which comes from the fast decomposition of 1,3-epoxycyclohexane.[8] Lemaire et al.[14] quantified products in a rapid compression machine after the cool flame at 720 K; average experimental ratios between 1,2-epoxycyclohexane and hex-5-en-1-al and between 1,4-epoxycyclohexane and hex-5-en-1-al were 0.11 and 0.25, respectively. The simulation leads to ratios of 0.09 and 0.18, respectively. The good agreement with experimental data validates the ratios between rate constants of reactions involved in Scheme 3.

The oxidation of cyclohexane in a jet-stirred reactor was studied at intermediate temperatures by Voisin et al.[17] under 10 bar with a residence time of 0.5 s. Figure 4 presents the comparison between simulations and experimental profiles obtained as a function of the temperature in the case of reactants (Figure 4a), carbon oxides (Figure 4b), and unsaturated C_6 cyclic products (Figure 4c).

SCHEME 5: Four-Center Pericyclic Decomposition of 1,3-Epoxycyclohexane to Hex-5-en-1-al



Reactant conversion and product amounts are satisfactorily predicted by the simulations, validating both low-temperature rate constant calculated in this work and cyclohexyl decomposition rate constant evaluated in a previous study.[6] If the major primary product is cyclohexene, flow rate analysis shows that the low-temperature mechanism is of importance up to 950 K in these conditions. At 800 K, the major reaction channel remains the addition of O_2 to alkyl radicals. Thus, 56% of cyclohexyl radicals produces cyclohexyperoxy radicals while 23% reacts with oxygen, yielding cyclohexene and HO_2•, and 6% of cyclohexyl radicals decomposes by β-scission, producing linear 5-hexenyl radicals. About 16% of the flow of cyclohexylperoxy radical isomerizes to 2-hydroperoxycyclohexyl radical (compound **3** in Scheme 3), 73% to 3-hydroperoxycyclohexyl radical (**4**), 10% to 4-hydroperoxycyclohexyl radical (**5**), and 1% produces cyclohexanone (**6**) and •OH. Hydroperoxycyclohexyl radicals decompose completely to hydroxyl radicals and

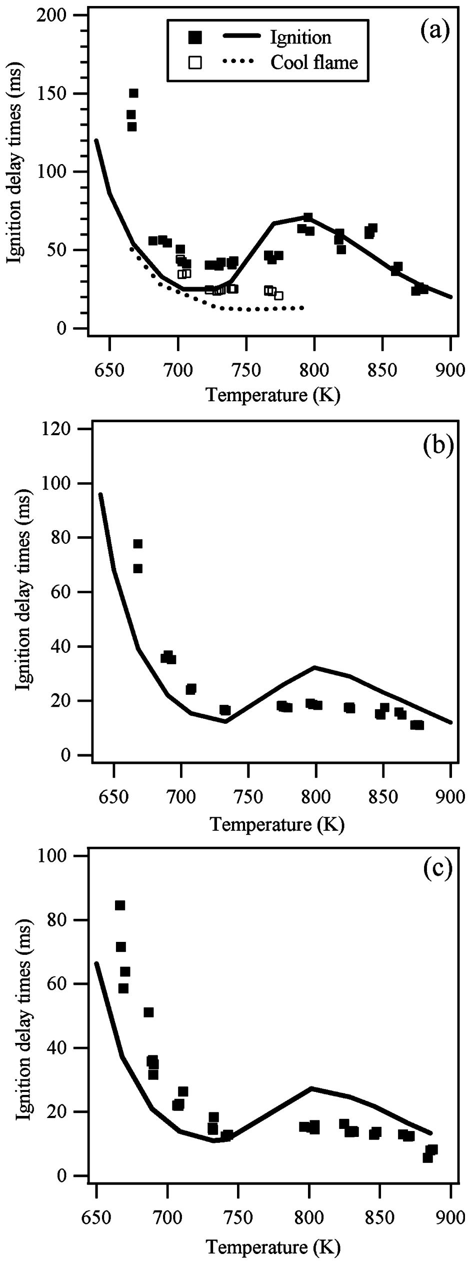


Figure 3. Comparison between experimental and simulated autoignition and cool flame delay times in a rapid compression machine[14] for stoichiometric mixtures (a) from 7.2 to 9.2 bar (initial pressure 350 Torr), (b) from 11.4 to 14.3 bar (initial pressure of 550 Torr), and (c) from 12.5 to 16.3 bar (initial pressure of 600 Torr). 650 K < T < 900 K. Points refer to experimental observations, while curves correspond to simulations.

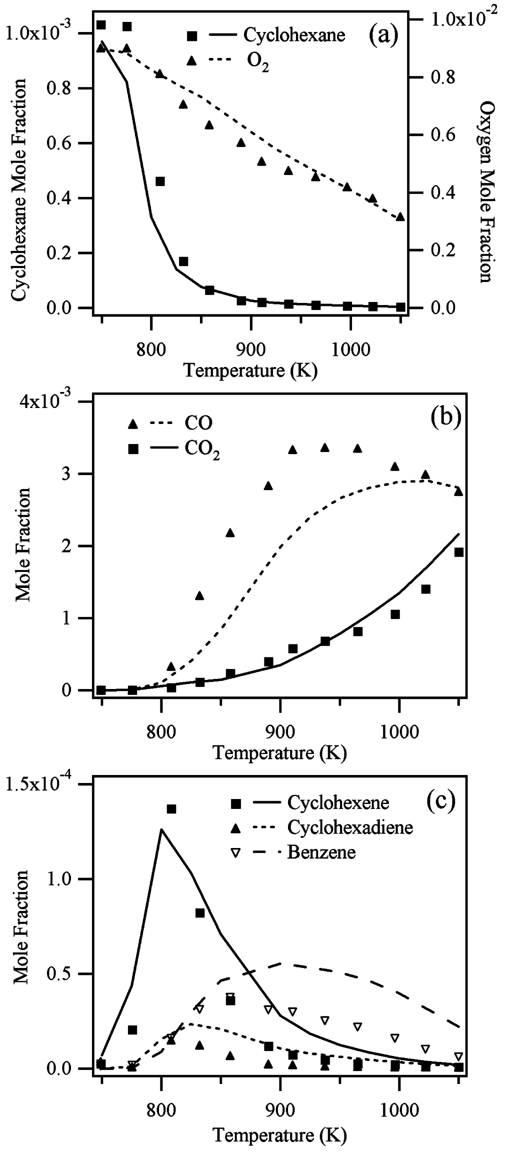


Figure 4. Comparison between experimental and simulated profiles of reactants and selected products in the oxidation of cyclohexane in a jet-stirred reactor[17] for stoichiometric mixtures under 10 bar with a residence time of 0.5s. Points refer to experimental observations while curves correspond to simulations.

cyclic ethers and hex-5-en-1-al. Less than 0.5% of the hydroperoxycyclohexyl radical flow produces •OOQOOH radicals, which ultimately yield ketohydroperoxides. Thus, the low-temperature mechanism does not lead to formation of branching agents at this intermediate temperature.

However, this pathway has a marked promoting effect on the global reaction rate, since it is competing with inhibiting reactions. Indeed, reaction of cyclohexyl radicals with O_2 yielding cyclohexene and HO_2• decreases strongly the global reactivity, since unreactive hydroperoxyl radicals react mostly by self-combination: $HO_2• + HO_2• \rightarrow H_2O_2 + O_2$. Since H_2O_2 decomposition is slow below 900 K, the latter reaction represents a termination step. The other competing reaction is the decomposition of cyclohexyl radicals by C−C bond breaking, yielding linear 5-hexenyl radicals. The main consumption route of this compound in an internal H-abstraction through a five-member ring transition state producing low-reactivity resonance-stabilized 2-hexenyl radical, which inhibits the combustion reaction. On the contrary, O_2 addition to cyclohexyl radicals leads ultimately to the formation of oxygenated compounds plus •OH radicals. This last species is extremely reactive and acts as the chain carrier in the combustion reaction. At this intermediate temperature, the low-temperature mechanism is no longer responsible for the formation of branching agents but allows a fast propagation, producing •OH radicals from cyclohexyl radicals.

At higher temperatures, the relative importance of the formation of cyclohexylperoxy radicals in the consumption of •C_6H_{11} radicals decreases. At 850 K, this pathway constitutes 34% of the flow, 14% at 900 K, and still 1.2% at 1000 K. Since the rate of decomposition by β-scission of cyclohexyl radicals increases strongly, the direct formation of cyclohexene and HO_2• drops off too, with a relative flow of 24%, 11%, and 1.5% at 850, 900, and 1000 K, respectively. Decompositions by β-scission become the most important reaction channels with an increasing proportion of C−H bond breaking yielding cyclohexene and H atom. Representing 2% of the consumption of •C_6H_{11} radicals at 800 K, the flow goes up to 7% at 850 K, 15% at 900 K, and 23% at 1000 K, while that of C−C bond breaking is 17%, 39%, 60%, and 74%, respectively, for the same temperatures. The ratio between C−H and C−C bond breaking increases then from 0.14 at 800 K to 0.31 at 1000 K. Contrary to the ring-opening, the formation of cyclohexene and H-atom has a promoting effect when temperature increases, since H atoms react in the branching step $•H + O_2 = •OH + •O•$. At low temperature, H-atoms react mostly with O_2, yielding unreactive HO_2• radical. At higher temperatures, the ratio between the formation of •OH + •O• and that of HO_2• increases: at 800 K, this ratio is equal to 0.013 but reaches 0.045 at 900 K and 0.12 at 1000 K. In the high-temperature range, the branching reaction is the most sensitive step.

These flow rate analyses lead to two important remarks that can be useful for future model developments and simulation. While the low-temperature mechanism (i.e., O_2 addition to cycloalkyl radicals) must obviously be taken into account for simulations below and within the NTC range, it still should be considered at intermediate temperatures as high as 950 K. Even if the flow of cyclohexylperoxy radicals becomes a minority, kinetic effects remain important and cannot be neglected in simulations below 950 K. Similar conclusions were also reached in the case of alkane oxidation.[38] The second remark concerns the role of C−H bond breaking, which is shown to be important even in the intermediate temperature range, where it is often neglected. Again, a minor reaction flow implies an important kinetic effect.

Conclusion

The isomerization−decomposition reactions of cyclopentylperoxy and cyclohexylperoxy radicals have been theoretically investigated at the CBS-QB3 quantum chemical level. Thermochemical and kinetic data have been calculated. In the isomerization reaction steps, the computed energy barriers are rather different from those estimated with usual semiempirical methods because of the particular structural characteristics of the bicyclic transition states that imply important changes in ring strain energies. In the case of cyclohexylperoxy radicals, for which few kinetic data were available in the literature, calculations are in a good agreement with values derived from experiments and other theoretical calculations. The theoretical data obtained in the present work, together with some results previously reported for the decomposition of cyclohexyl radicals, have been introduced in the reaction model of Buda et al.[11] The upgraded model is able to reproduce experimental data from Lemaire et al.[14] at low temperature and from Voisin et al.[17] in the intermediate temperature range. No adjustment of the rate constant of the cyclohexyl + O_2 reaction was necessary, in contrast to the investigation of Buda et al. The study of cycloalkylperoxy radicals reactions can now be extended to alkylcyclohexanes, which are contained in large amounts in most usual fuels.

Acknowledgment. The Centre Informatique National de l'Enseignement Supérieur (CINES) is gratefully acknowledged for allocation of computational resources.

Supporting Information Available: Full list of authors in ref 24, structural parameters, and energies for all species investigated in our study, as well as the mechanism for the oxidation of cyclohexane. This material is available free of charge via the Internet at http://pubs.acs.org.

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