

Pressure-dependent rate rules for intramolecular H-migration reaction of Hydroperoxyalkylperoxy radicals in low temperature

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Introduction

Combustion modeling with chemical kinetic mechanisms is important to predict the combustion properties and combustion products for a new or nontraditional fuels. Usually, the kinetic mechanisms for the combustion of hydrocarbon fuels are expected to be suitable for a wide range of temperatures and pressures. The oxidative regions can be classified as low-, intermediate-, and high-temperature oxidative regions of hydrocarbon fuels. Currently, combustion mechanisms of hydrocarbon fuels are well developed for the high-temperature oxidative regions.[1-3] Construction of detailed mechanisms for low-temperature combustion is more difficult than for high-temperature combustion as these mechanisms contain a large number of oxygen-containing reaction classes and considerable uncertainty of the kinetic parameters remains. Among these oxygen-containing reaction classes, intramolecular isomerization reaction class of hydroperoxyalkylperoxy radicals ($\bullet\text{O}_2\text{QOOH}$) is one of the most important reaction classes and up to now, few studies are carried out on this class[4-6]. The internal transfer of a hydrogen atom in $\bullet\text{O}_2\text{QOOH}$ radical which is a reversible reaction can form a dihydroperoxyl radical and the subsequent decomposition of this radical into keto-hydroperoxides occurs simultaneously. The formation and decomposition of keto-hydroperoxides is a chain branching process because it produces three radicals (two $\bullet\text{OH}$ radicals and one alkoxy radical).

The purpose of this study is to get more accurate rate rules for the intra-molecular H-shift reactions of $\bullet\text{O}_2\text{QOOH}$ radicals: (1) The reactions are divided into classes according to the ring size of the transition states and the types of the carbons from which the H atom is transferred. Meanwhile, rate rules are given not only for $-\text{OOH}$ bonded carbon, but also for non- $-\text{OOH}$ bonded carbon; (2) Rate rules are obtained by the average of some representative reactions, instead of from the minimum-sized representative reaction; (3) Evans-Polanyi relationships for each class of the intramolecular H-migration reactions of $\bullet\text{O}_2\text{QOOH}$ radicals are studied; (4) Influence of the molecular sizes on the pressure-dependent rate constants and rate rules for the pressure-dependent rate constants of the unimolecular isomerization are studied.

Computational details

The geometries of all reactants, intermediates, products and tight transition states (TS) are optimized at the level of MP2/CBSB7. The vibrational frequencies are calculated at the same level and scaled by a factor of 0.97 for the calculation of zero point energy (ZPE). The single point energy for all stationary geometries and transition states are obtained by

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composite CBS-QB3 method and the coordinate of all the species are frozen in the optimization.

All the rate constant calculations are performed by using ChemRate software. Pressure dependent rate constants are determined using the RRKM/ME methodology proposed by Miller and Klippenstein. All master equation calculations are performed at temperatures between 500 and 1200 K and pressures between 0.01 and 1000 atm of Ar diluent.

Results and Discussion

Rate constants for all reactions for $-OOH$ bonded case according to rate rules are shown in Figure 1. It can be seen that the curves for (1,n)t always lie above the curves for (1,n)s for the same n, indicating that the rate constants increase with the numbers of the substitution groups for reactions with same ring size of the transition state. This is generally because that the substituent groups connected to the carbon neighbor to $-OOH$ group can stabilize the transition state and lower energy barriers.

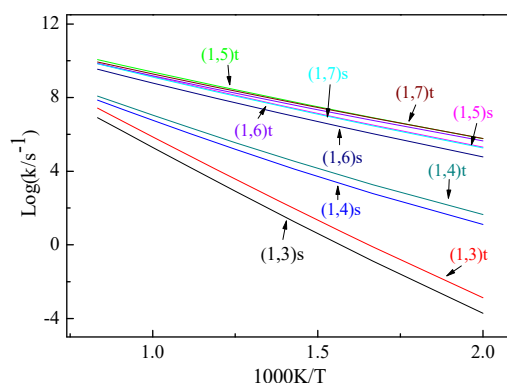


Figure 1. Comparison of rate rules of 1,3- to 1,7-H shift reactions for $-OOH$ bonded case at 500-1200K.

Comparison of the pressure dependent rate constants for 1,4-H migration reaction $O_2C(C)COO\bullet \rightarrow O_2C(C\bullet)COO$ calculated in this study with the results calculated by Goldsmith et al.[4] is shown in Figure 2. It can be seen that the pressure dependence in the two results shows opposite trends: our results show that the rate constants for this reaction increase with pressure, while Goldsmith et al's results show that the rate constants decrease with pressure. This reaction is a unimolecular isomerization reaction and the rate constants should increase with pressure, indicating our results are reasonable.

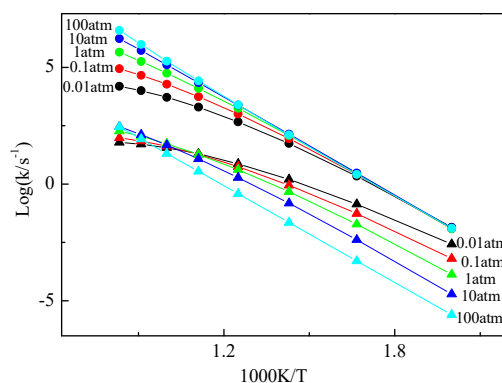


Fig. 2. Pressure dependent rate constants of 1,4-H migration reaction $O_2C(C)COO\bullet \rightarrow O_2C(C\bullet)COO$. \blacktriangle represents the rate constants calculated by Goldsmith et al.,[4] \bullet represents the rate constants calculated in this study.

The Evans-Polanyi plots for the intramolecular H-migrations reactions of $\bullet O_2QOOH$ radicals are shown in Figure 3. The fits for the 1,3-, 1,4-, 1,5-, 1,6- and 1,7-H migration reactions for $-OOH$ bonded case are $E=0.84\Delta H + 33.17$, $E=1.57\Delta H + 11.67$, $E=0.78\Delta H + 9.76$, $E=1.04\Delta H + 6.63$ and $E=0.56\Delta H + 11.90$, respectively. The fits of the 1,4-, 1,5-, 1,6- and 1,7-H migration reactions for non- $-OOH$ bonded case are $E=1.15\Delta H + 16.87$, $E=0.84\Delta H + 9.61$, $E=1.02\Delta H + 7.54$ and $E=1.18\Delta H + 4.96$, respectively. The slopes of these graphs are ≈ 1 for all of the ring sizes.

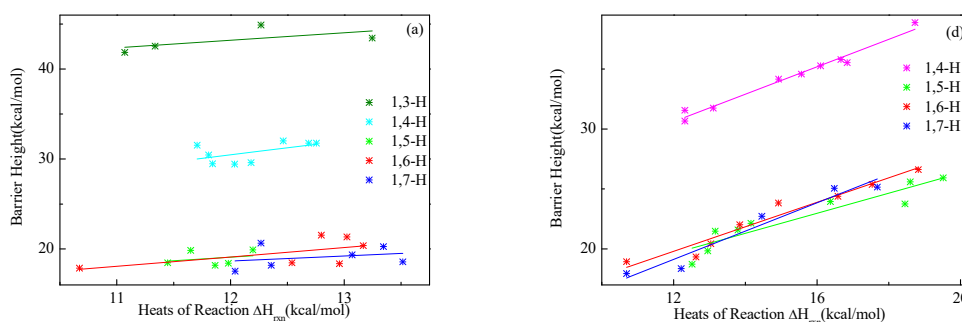
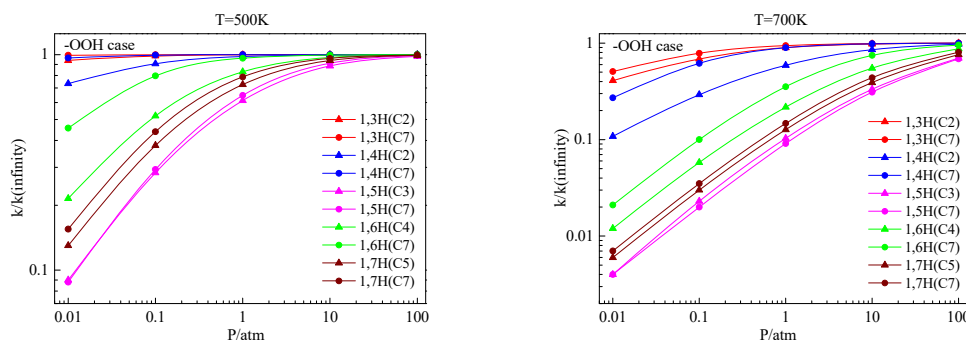


Fig. 3. Evans-Polanyi plots for the intramolecular H-migration reactions of $\bullet O_2QOOH$ radicals. (a) The reactions of H atom shift from $-OOH$ bonded carbon. (b) The reactions of H atom shift from non- $-OOH$ bonded carbon.

In kinetic models, gas-phase reactions involving large molecules are often assumed to be in the high-pressure limit. Molecular size dependence of the rate constants of the intramolecular H shift reactions of $\bullet O_2QOOH$ radicals in the fall-off regime are studied in this work. The ratios $k(T,P)/k_\infty(T)$, while $k(T,P)$ is the temperature and pressure-dependent rate constant and $k_\infty(T)$ is high-pressure limit rate constant. For illustration of the impact of molecular size on the pressure dependent rate constants, Figure 4 plots the ratios $k(T,P)/k_\infty(T)$ for the smallest reactions and the largest reactions considered for $-OOH$ bonded case and non- $-OOH$ bonded case in each ring-size class. It can be seen that the pressure dependence of the rate constants of intramolecular H-migration reactions of $\bullet O_2QOOH$ radicals decreases with the molecular size and barrier height at low temperatures and the impact of molecular size on the pressure-dependent rate constants decrease as temperature increases. The pressure dependence for these reactions cannot be ignored and the influence of pressure on the rate constant is increasing as temperature increases and it becomes significant at the temperature larger than 700K.



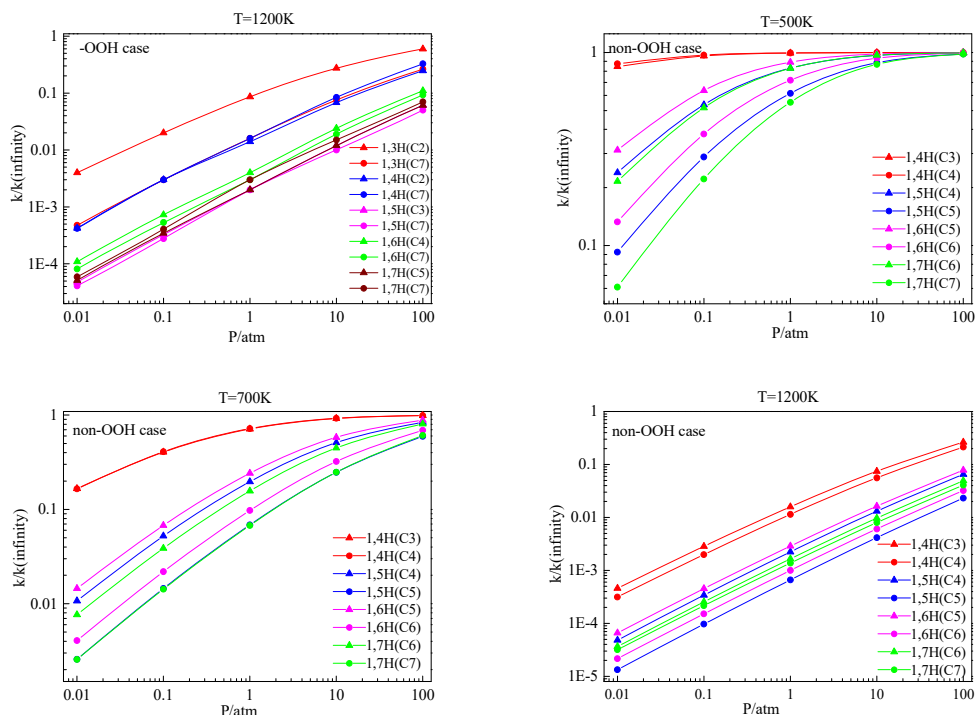


Fig. 4. The ratios $k(T,P)/k_{\infty}(T)$ for represented reactions.

Conclusions

In this work, the rate constants of the important reaction class of the intramolecular H-migration reactions of $\bullet\text{O}_2\text{QOOH}$ radicals at 500-1200 K have been investigated. The high pressure limit rate rules are derived by taking the average of the rate constants from a representative set of reactions with different sizes of the substitutes. The intramolecular H-migration reactions of $\bullet\text{O}_2\text{QOOH}$ radicals are pressure dependent and the influence of pressure on the rate constants increases as temperature increases. It is shown that the pressure dependence of the rate constants of intramolecular H-migration reactions decreases with the molecular size and barrier height at low temperatures and the impact of molecular size on the pressure-dependent rate constants decreases as temperature increases. The pressure-dependent rate rules are derived by taking the average of the rate constants from a representative set of reactions with different sizes of the substitutes at the same pressure.

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