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Article

Catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen: Determination of autoxidation temperature and product distribution☆



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ABSTRACT

Autoxidation of cycloalkanes (C5–C8) with molecular oxygen under catalyst-free and solvent-free conditions was conducted systematically for the first time, focusing on the autoxidation temperature and product distribution. The autoxidation of cyclopentane, cyclohexane, cycloheptane and cyclooctane occurs at 120 °C, 130 °C, 120 °C, and 105 °C respectively, with obvious oxidized products formation. At 140 °C, 145 °C, 130 °C and 125 °C, acceptable yields of the oxidized products could be obtained for them, and the oxidized product distributions were investigated in detail. The autoxidation of cycloalkanes follows the pseudo-first-order kinetic model and the apparent activation energies (E_a) for the autoxidation of cyclopentane and cyclohexane are 159.76 kJ·mol⁻¹ and 86.75 kJ·mol⁻¹ respectively. This study can act as an important reference in screen of suitable reaction temperature and comparison of the performance of various catalysts in the catalytic oxidation of cycloalkanes in the attempt to enhance the oxidized product selectivity.

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1. Introduction

The oxidation of cycloalkanes to corresponding cycloalkanols, cycloalkanones and aliphatic diacids is an extremely important chemical transformation not only in chemical industry but also in academic research, especially for cyclohexane [1–9]. In the oxidation of cyclohexane, the obtained cyclohexanol and cyclohexanone are very important intermediates in the production of caprolactam, and adipic acid which is the irreplaceable precursor in the production of nylon-66 and nylon-6 polymers [10–19]. Glutaric acid, heptanedioic acid and octanedioic acid obtained from oxidation of the corresponding cycloalkane directly or indirectly are important precursors in the production of various macromolecule polymers too [20–24]. In addition, cycloalkanols and cycloalkanones are important intermediates and solvents in the chemical industry and academic research [25–31]. To realize this necessary transformation from cycloalkanes to their oxidized products, several oxidants can be employed, such as iodosylbenzene [32–38], iodosylbenzene diacetate [34,38–40], tert-butyl hydroperoxide [41–49], m-chloroperoxybenzoic acid [50–55], hydrogen peroxide [56–63], molecular oxygen [64–72], ozone [73,74], and so on. Among

these oxidants, molecular oxygen is considered as the most promising choice from the perspective of Green Chemistry, which is inexpensive, readily available, and environmentally benign with harmless water as the only by-product. In current industrial process, the oxidation of cyclohexane is conducted at 150–170 °C and 1.0–2.0 MPa pressure using homogeneous cobalt salt as catalyst and molecular oxygen as oxidant, and in order to improve the selectivity of desired products (cyclohexanol and cyclohexanone), the conversion of cyclohexane is usually kept at 3%–8% with an acceptable selectivity towards cyclohexanol and cyclohexanone, 80%–85% [12,18,47,75–78]. The main drawbacks of the current industrial process are the high temperature, low conversion, low selectivity and low yield, especially the high temperature which induces the oxidation of cyclohexane to process through uncatalyzed and unselective free radical autoxidation pathways, resulting in the low selectivity [75]. In order to smooth the transformation from cycloalkanes to their oxidized products employing molecular oxygen as oxidant, several catalytic systems have been explored, such as transition metal complex catalysis [8–81], metal nanoparticle catalysis [68–72,82,83], metal oxide nanoparticle catalysis [3,16], molecular sieve catalysis [84–86], carbon material catalysis [69, 87,88], photocatalysis [9,71,89], and so on. Although the conversion of cycloalkanes and the selectivity of desired oxidized products are improved obviously under the catalytic condition, the reaction temperature still stays at about 150 °C in most of the oxidation systems, and the obtained oxidized products still is a mixture of cycloalkanols and cycloalkanones, even some aliphatic diacids [8,70,72,80–82,86]. At so

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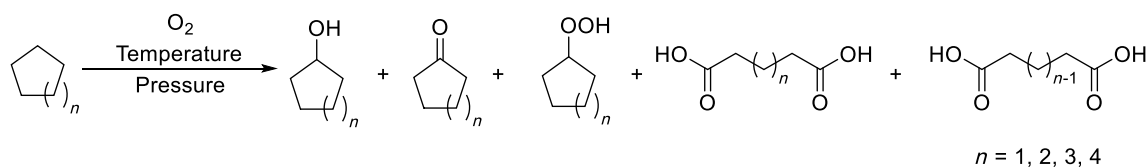
high temperature, the oxidation of cycloalkanes at the presence of molecular oxygen as oxidant processes through both catalytic oxidation pathway and autoxidation pathway which is unselective and limits the improvement in the selectivity. How to eliminate the autoxidation in the catalytic oxidation of cycloalkanes is an enormous challenge in the precise adjustment of the product formation.

In our attempt to adjust the product formation precisely in the oxidation of cyclohexane using metalloporphyrin as catalyst and molecular oxygen as oxidant [90–95], it was found that, in most of the catalytic systems reported at present, the oxidation of cyclohexane processed through both catalytic oxidation pathway and autoxidation pathway because of the high reaction temperature, resulting in low selectivity [8,70,72,80–82,86]. The high reaction temperature is the origin of the autoxidation. It may be a good choice to conduct the oxidation of cycloalkanes at lower temperature to avoid the unselective autoxidation and enhance the desired product selectivity through catalytic oxidation pathway. To the best of our knowledge, there is not a clear document at present involved in the temperature at which the autoxidation of cycloalkanes using molecular oxygen as oxidant would

occur, no document distinguishing the autoxidation from the catalytic oxidation in the oxidation of cycloalkanes through reaction temperature control clearly. Thus in this work, we investigate the catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen systematically, focusing on the autoxidation temperature and product distribution, which will act as an important reference in screen of suitable reaction temperature and comparison of the performance of various catalysts in the catalytic oxidation of cycloalkanes.

2. Results and Discussion

In this work, the oxidation of cycloalkanes using molecular oxygen as oxidant under catalyst-free and solvent-free condition was conducted in a 100-ml autoclave reactor equipped with an inner Teflon liner and a magnetic stirrer. Cyclopentane, cyclohexane, cycloheptane and cyclooctane were selected as substrates as shown in Scheme 1 for their ready availability and the high values of their oxidized products. All the oxidized products which can be detected on GC and HPLC were analyzed quantitatively in order to investigate the autoxidation



Scheme 1. Catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen.

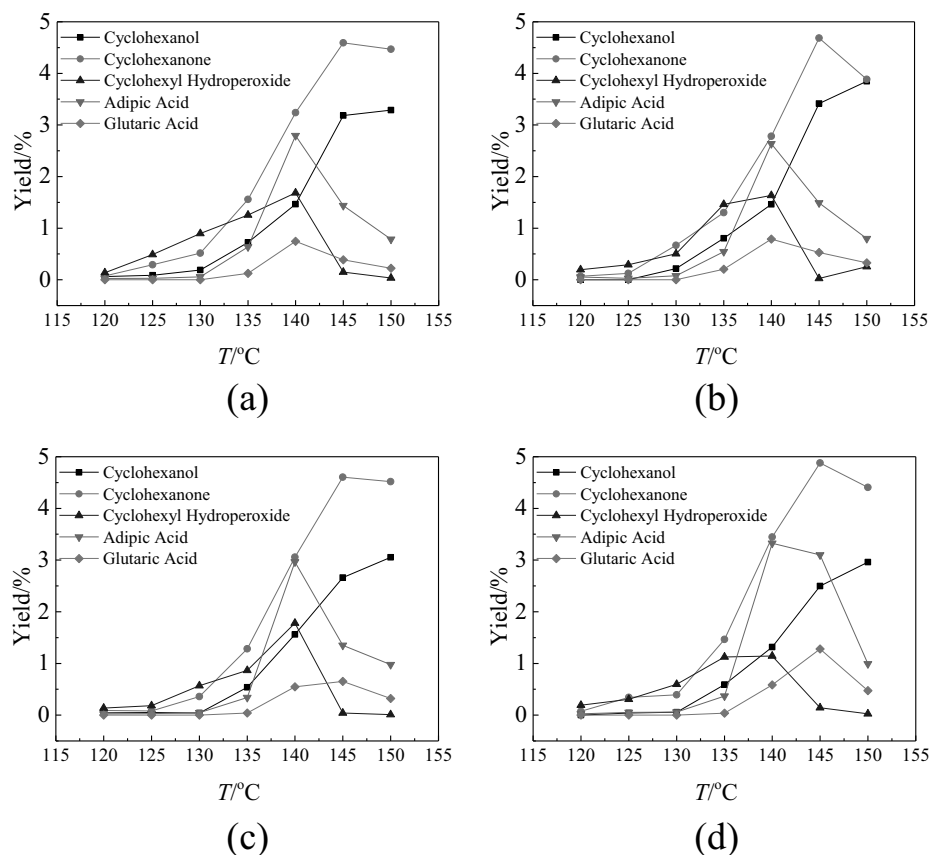


Fig. 1. Effect of reaction temperature on the autoxidation of cyclohexane. Reaction condition: cyclohexane (200 mmol, 16.8320 g), O₂ (a. 1.0 MPa, b. 1.2 MPa, c. 1.6 MPa, d. 1.8 MPa), 8.0 h. The yields of cyclohexanol and cyclohexanone were determined by GC after treatment with PPh₃ employing toluene as internal standard, and the yield of cyclohexyl hydroperoxide was determined through the amount of O = PPh₃ obtained from reduction of cyclohexyl hydroperoxide with PPh₃. The yield of adipic acid and glutaric acid were determined by HPLC with benzoic acid as internal standard.

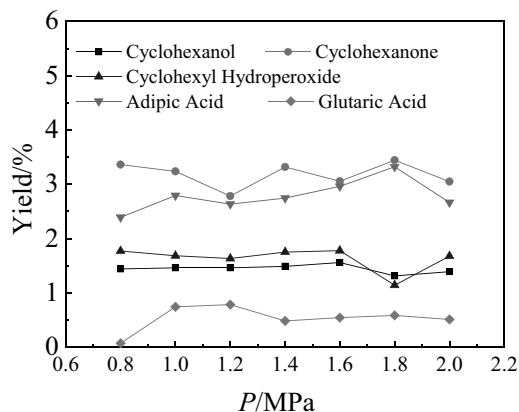


Fig. 2. Effect of reaction pressure on the autoxidation of cyclohexane. Reaction condition: cyclohexane (200 mmol, 16.8320 g), O_2 , 140 °C, 8.0 h. The yields of cyclohexanol and cyclohexanone were determined by GC after treatment with PPh_3 employing toluene as internal standard, and the yield of cyclohexyl hydroperoxide was determined through the amount of $O = PPh_3$ obtained from reduction of cyclohexyl hydroperoxide with PPh_3 . The yield of adipic acid and glutaric acid were determined by HPLC with benzoic acid as internal standard.

performance of various cycloalkanes in detail, including cycloalkanols, cycloalkanones, cycloalkyl hydroperoxide, aliphatic diacids with the same and one less carbon number compared with parent cycloalkanes. Firstly, catalyst-free and solvent-free oxidation of cyclohexane was carried out at the temperature ranging from 120 °C to 150 °C and the pressure ranging from 0.80 MPa to 2.0 MPa based on some exploratory experiments. The reaction time was selected as 8.0 h in order to achieve obvious oxidized products formation indicated in Fig. S4. As shown in

Figs. 1, 2 and Figs. S1–S3, it is obvious that the reaction temperature plays the most critical role in the autoxidation of cyclohexane compared to reaction pressure. When the reaction temperature was 120 °C, no obvious oxidized product formed. As the reaction temperature increased, the autoxidation of cyclohexane occurred at about 130 °C with obvious oxidized products formation. When the temperature reached 145 °C, acceptable yields of oxidized products could be obtained, cyclohexanol (3.18%), cyclohexanone (4.59%), cyclohexyl hydroperoxide (0.15%), adipic acid (1.44%) and glutaric acid (0.39%) under 1.0-MPa O_2 pressure, and no other obvious product was detected in the liquid and solid reaction mixture. The yields of the oxidized products at 145 °C and 1.0 MPa increase as following: cyclohexyl hydroperoxide (0.15%) < glutaric acid (0.39%) < adipic acid (1.44%) < cyclohexanol (3.18%) < cyclohexanone (4.59%). The reaction temperature also affected the oxidized product distribution remarkably. For example, at 140 °C and 1.0 MPa, the product distribution is very different from 145 °C, and the yields of the products increase as following: glutaric acid < cyclohexanol < cyclohexyl hydroperoxide < adipic acid < cyclohexanone. The yield of glutaric acid becomes the lowest one instead of cyclohexyl hydroperoxide, and the yield of cyclohexanone still is the highest one. As for the reaction pressure, it does not seem to have significant effect on the autoxidation of cyclohexane as indicated in Fig. 2 and Fig. S5, which just supplies enough oxygen to the oxidation system.

Then based on the results obtained from the autoxidation of cyclohexane, the substrates were extended to cyclopentane, cycloheptane and cyclooctane. The results were listed in Fig. 3. It is demonstrated that the autoxidation temperatures are 120 °C, 120 °C and 105 °C for cyclopentane, cycloheptane and cyclooctane respectively, at which obvious oxidized products could be detected. For cyclopentane, acceptable yields of oxidized products could be achieved at 140 °C, and the yields of the oxidized products increase as following: cyclopentyl

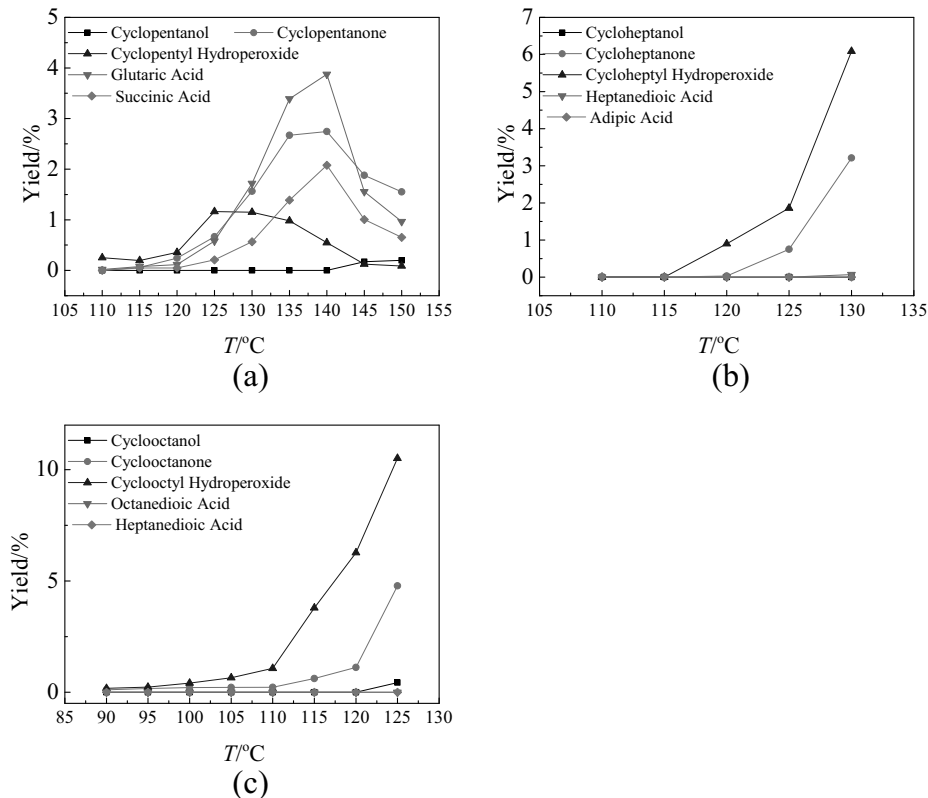


Fig. 3. Effect of reaction temperature on the autoxidation of cyclopentane (a), cycloheptane (b) and cyclooctane (c). Reaction condition: a. cyclopentane (200 mmol, 14.0260 g), O_2 (1.6 MPa), 8.0 h. b. cycloheptane (200 mmol, 19.6380 g), O_2 (0.6 MPa), 8.0 h. c. cyclooctane (200 mmol, 22.4440 g), O_2 (0.6 MPa), 8.0 h. The yields of cycloalkanol and cycloalkanone were determined by GC after treatment with PPh_3 employing toluene as internal standard, and the yield of cycloalkyl hydroperoxide was determined through the amount of $O = PPh_3$ obtained from reduction of cycloalkyl hydroperoxide with PPh_3 . The yield of aliphatic diacids was determined by HPLC with benzoic acid as internal standard.

hydroperoxide (0.55%) < succinic acid (2.08%) < cyclopentanone (2.75%) < glutaric acid (3.88%), no obvious cyclopentanol being detected in the reaction mixture. Compared with cyclohexane, the yield of the aliphatic diacid possessing the same carbon number with parent cycloalkane became the highest one in the autoxidation of cyclopentane for its high strain energy. As for cycloheptane and cyclooctane, satisfying yields of oxidized products could be obtained at 130 °C and 125 °C respectively, and the products were mainly cycloalkyl hydroperoxides and cycloalkanones, no obvious cycloalkanol and diacid being detected. The yield of cycloalkyl hydroperoxide was higher than cycloalkanone in both autoxidation of cycloheptane and cyclooctane. The reason why the autoxidation of cycloheptane and cyclooctane were not conducted at higher reaction temperature is that the autoxidation process would become uncontrollable and the reaction temperature would be runaway to above 170 °C at higher initial reaction temperature.

Thus, it is clear that the autoxidation of cycloalkanes under catalyst-free and solvent-free condition could be achieved at the temperature of 120 °C, 130 °C, 120 °C, and 105 °C for cyclopentane, cyclohexane, cycloheptane and cyclooctane respectively, with obvious oxidized products formation. Acceptable yields of the oxidized products could be obtained at 140 °C, 145 °C, 130 °C and 125 °C for cyclopentane, cyclohexane, cycloheptane and cyclooctane respectively. For cyclopentane, the product distribution at 140 °C increased as following: cyclopentyl hydroperoxide (0.55%) < succinic acid (2.08%) < cyclopentanone (2.75%) < glutaric acid (3.88%), no obvious cyclopentanol being detected. For cyclohexane, the product distribution at 145 °C increased as following: cyclohexyl hydroperoxide (0.15%) < glutaric acid (0.39%) < adipic acid (1.44%) < cyclohexanol (3.18%) < cyclohexanone (4.59%), and for cycloheptane and cyclooctane, the products were cycloalkyl hydroperoxides and cycloalkanones mainly, no obvious cycloalkanol and diacid being detected. The yield of cycloalkyl hydroperoxide is higher than cycloalkanone. It is also demonstrated that the autoxidation existed in most of the current catalytic oxidation of cycloalkanes indeed, especially in the oxidation of cyclohexane in which the reaction temperature is about 150 °C [8,70,72,80–82,86]. Therefore, it could be a good choice and a meaningful reference to conduct the catalytic oxidation of cycloalkanes below the autoxidation temperature, so the reaction can process smoothly and selectively. Taking into account the security, it is also suggested that (1) the autoxidation of cycloalkanes should be conducted in the autoclave reactor equipped with an inner Teflon liner to avoid the existence of any catalytic metal, which could induce the autoxidation process too severely to explode; (2) the autoxidation temperature should be below 150 °C to avoid the possible

explosion; (3) the autoxidation pressure should be below 2.0 MPa to avoid the possible explosion.

At last, the kinetics of the autoxidation of cycloalkanes were investigated employing cyclopentane and cyclohexane as model substrates based on the results obtained in the autoxidation of cycloalkanes above. It was found that the pseudo-first-order kinetic model fitted the autoxidation of cyclopentane and cyclohexane well, which is expressed as following: $-\ln(C_A/C_{A0}) = kt$, where C_{A0} is the initial concentration of cycloalkane; C_A is the concentration of cycloalkane at time t ; k is the pseudo-first-order rate constant (h^{-1}). The plots of $-\ln(C_A/C_{A0})$ versus t at 130 °C, 135 °C, 140 °C are presented in Fig. 4 and from the slope of the plots, the pseudo-first-order rate constant k for the autoxidation of cyclopentane and cyclohexane at 130 °C, 135 °C, 140 °C were obtained as shown in Table 1. Then the plots of

Table 1

The pseudo-first-order kinetic parameters for the autoxidation of cyclopentane and cyclohexane at 130 °C, 135 °C, 140 °C

$T/^\circ\text{C}$	Cyclopentane		Cyclohexane	
	k/h^{-1}	R^2	k/h^{-1}	R^2
130	0.00600	0.9637	0.00180	0.9724
140	0.01217	0.9226	0.00227	0.9617
150	0.01900	0.9592	0.00337	0.9850

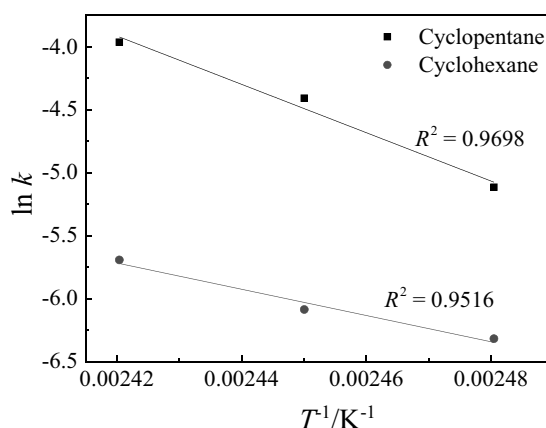


Fig. 5. Plots of $\ln k$ versus $1/T$ for the autoxidation of cyclopentane and cyclohexane.

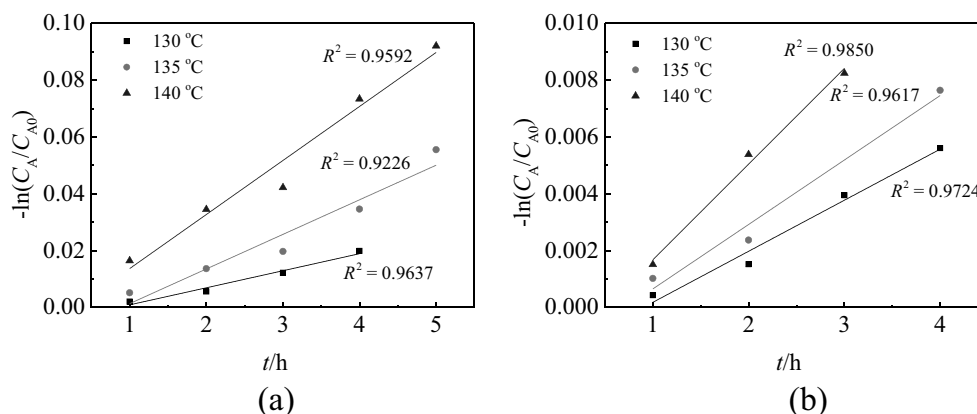


Fig. 4. Pseudo-first-order fit for the autoxidation of cyclopentane (a) and cyclohexane (b) at 130 °C, 135 °C, 140 °C. Reaction condition: cycloalkane (100 mmol), O_2 (1.6 MPa). The yields of cycloalkanol and cycloalkanone were determined by GC after treatment with PPh_3 employing toluene as internal standard, and the yield of cycloalkyl hydroperoxide was determined through the amount of $\text{O} = \text{PPh}_3$ obtained from reduction of cycloalkyl hydroperoxide with PPh_3 . The yields of aliphatic diacids were determined by HPLC with benzoic acid as internal standard.

$\ln k$ versus $1/T$ were listed in Fig. 5 and the apparent activation energies (E_a) for the autoxidation of cyclopentane and cyclohexane could be obtained from the slope following equation $\ln k = -(E_a/R) \times (1/T) + \ln k_0$, which were $159.76 \text{ kJ} \cdot \text{mol}^{-1}$ and $86.75 \text{ kJ} \cdot \text{mol}^{-1}$ for cyclopentane and cyclohexane respectively.

3. Conclusions

In conclusion, catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen was conducted systematically for the first time, focusing on the determination of autoxidation temperature and product distribution. It is obvious that the reaction temperature plays the most critical role in the autoxidation of cycloalkanes compared to reaction pressure and the autoxidation occurs at 120°C , 130°C , 120°C , and 105°C for cyclopentane, cyclohexane, cycloheptane and cyclooctane respectively, with obvious oxidized products formation. Acceptable yields of the oxidized products could be obtained at 140°C , 145°C , 130°C and 125°C respectively for them, and the oxidized products distribution for cyclopentane increased as following: cyclopentyl hydroperoxide (0.55%) < succinic acid (2.08%) < cyclopentanone (2.75%) < glutaric acid (3.88%) at 140°C , no obvious cyclopentanol being detected; the yields of the oxidized products for cyclohexane increased as following: cyclohexyl hydroperoxide (0.15%) < glutaric acid (0.39%) < adipic acid (1.44%) < cyclohexanol (3.18%) < cyclohexanone (4.59%) at 145°C ; for cycloheptane and cyclooctane, the products were mainly cycloalkyl hydroperoxides and cycloalkanones, no obvious cycloalkanol and diacid being detected, cycloheptyl hydroperoxide (6.09%) > cycloheptanone (3.21%) at 130°C and cyclooctyl hydroperoxide (10.51%) > cyclooctanone (4.78%) at 125°C . At last, the autoxidation of cycloalkanes follow the pseudo-first-order kinetic model and the apparent activation energies (E_a) for the autoxidation of cyclopentane and cyclohexane are $159.76 \text{ kJ} \cdot \text{mol}^{-1}$ and $86.75 \text{ kJ} \cdot \text{mol}^{-1}$ respectively. To the best of our knowledge, this study is the first systematic document up to now which revealed the autoxidation temperature and product distribution of the catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen. This study will act as an important reference in screen of suitable reaction temperature and comparison of the performance of various catalysts in the catalytic oxidation of cycloalkanes in the attempt to enhance the oxidized product selectivity.

Supplementary Material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.cjche.2018.02.019>.

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