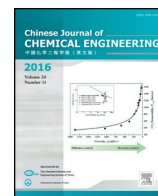




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Article

Catalyst-free and solvent-free oxidation of cycloalkanes (C5–C8) with molecular oxygen: Determination of autoxidation temperature and product distribution[☆]Haimin Shen, Yan Wang, Jinhui Deng, Long Zhang, Yuanbin She^{*}

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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 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

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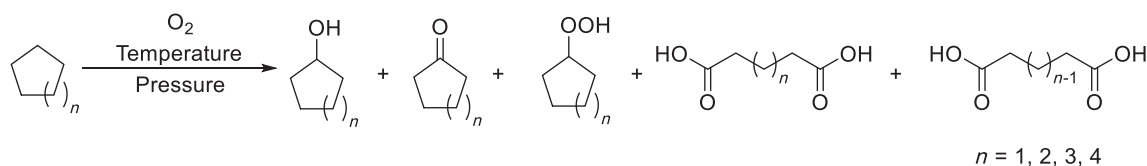
the catalytic oxidation of cycloalkanes is an enormous challenge in the precise adjustment of the product formation.

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 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 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



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

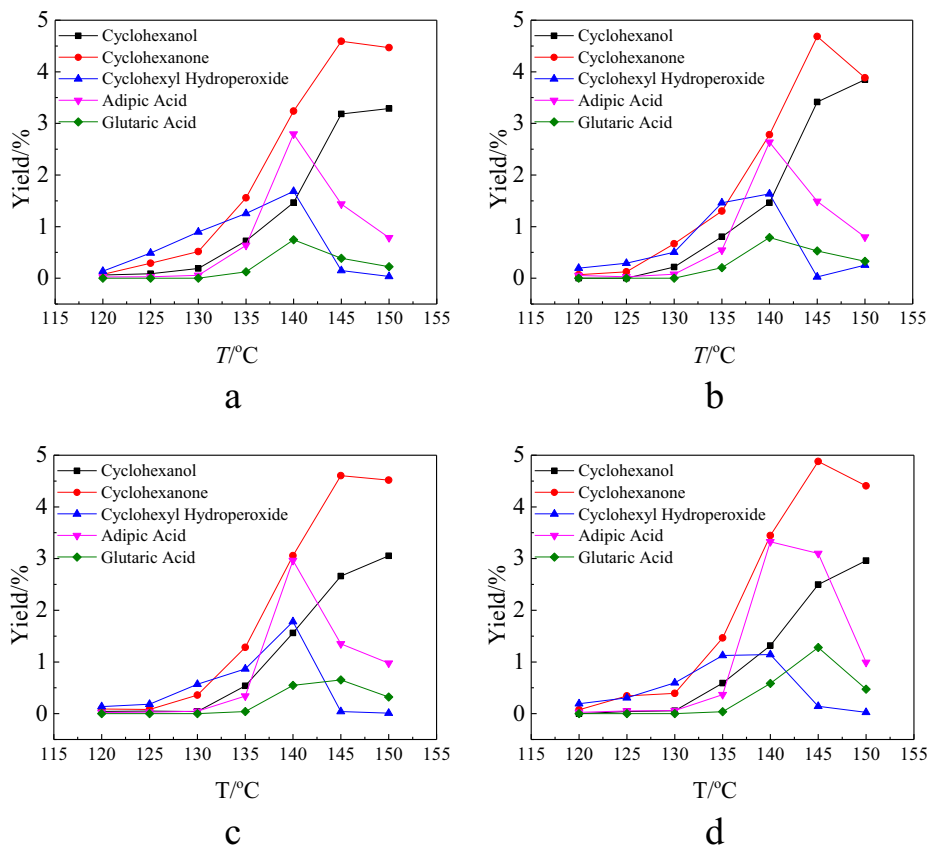


Fig. 1. Effect of reaction temperature on the autoxidation of cyclohexane. Reaction condition: cyclohexane (200 mmol, 16.8320 g), O₂ (a. 1.0 MPa, b. 1.2 MPa, c. 1.6 MPa, d. 1.8 MPa), 8.0 h. The yields of cyclohexanol and cyclohexanone were determined by GC after treatment with PPH₃ employing toluene 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.

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