



Short communication

The N-Hydroxyphthalimide catalyzed oxidation of cyclohexene to cyclohexenyl hydroperoxide: Reasons for deactivation and stability of the catalyst



N.I. Kuznetsova*, L.I. Kuznetsova, O.A. Yakovina, D.E. Babushkin, B.S. Bal'zhinimaev

Boreskov Institute of Catalysis SB RAS, Russia

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ABSTRACT

Selective oxidation of cyclohexene to cyclohexenyl hydroperoxide catalyzed by N-hydroxyphthalimide (NHPI) was studied. Kinetic observations and ^{13}C and ^1H NMR spectroscopy showed that accumulation of cyclohexenyl hydroperoxide was accompanied by deactivation of the catalyst. A mechanism of the deactivation through phthalimido N-oxyl radical (PINO) addition to vinyl position of olefin was suggested. Responsible for the deactivation, PINO- $\text{C}_6\text{H}_{10}\text{-OOH}$ hydroperoxide adducts were detected in the reaction conditions, and their molecular structure was elucidated by DFT technique. The mechanism explained an unexpected experimental effect, that is, lowering the oxygen partial pressure improved the stability of NHPI without decrease in production of cyclohexenyl hydroperoxide.

1. Introduction

Promising innovations in aerobic liquid-phase oxidation of hydrocarbons are currently associated with the application of organocatalysts. N-hydroxyphthalimide (NHPI) is an important and widely used member of this family, which is capable of catalyzing numerous free-radical oxidations [1–8]. The free-radical oxidation of hydrocarbons is initiated by hydrogen abstraction from NHPI to generate reactive phthalimido N-oxyl radical (PINO) (Reaction (1)). Reactions (2)–(4) form a catalytic cycle in which a hydrocarbon is converted to hydroperoxide.



The organic hydroperoxides are highly demanded reagents for synthesis of fine organics [9, 10]. Sheldon [11, 12] and other researches [13–16] achieved excellent results in the preparation of hydroperoxides derived from alkylbenzenes in the presence of NHPI catalyst. Similar information regarding olefins is not very extensive. The aerobic radical oxidation of olefins is usually directed to allylic position to form allyl hydroperoxides as primary products. Cyclohexene is the most susceptible to the allylic oxidation among light olefin [17]. In the absence of

catalyst, it forms 2-cyclohexen-1-yl hydroperoxide (CHHP), but the selectivity was as low as 50% at 6% conversion of cyclohexene [18]. Better selectivity to CHHP (80%) was achieved when the oxidation was carried out with 2,2'-azobis(2-methylpropionitrile) initiator [19]. Catalysis by NHPI is often resulted in formation of stable products, predominantly, allylic ketone. Ishii first performed the aerobic oxidation of cyclohexene with NHPI. 2-Cyclohexen-1-one and 2-cyclohexen-1-ol with overall selectivity of 43% were obtained at 70 °C in benzonitrile solution [1]. Later, NHPI was used together with anthraquinone [20] or more reactive 2,3-dichloro-5,6-dicyano-benzoquinone [21] promoters. CHHP was in both cases obtained as a minor product together with main product cyclohexen-1-one. In a recent study [22], NHPI catalyzed oxidation of cyclohexene to CHHP was performed at 35 °C. The oxidation was very slow, but substantially accelerated by UV-irradiation and addition of NI (naphthalene monoimide). Due to the photo-activation, the catalyst worked at the low temperature which in turn provided stability of CHHP. We tried to obtain CHHP from cyclohexene under conventional catalysis by NHPI and in the absence of any additives and metal components. Another issue that received little attention before was possible deactivation of NHPI during the oxidation of olefins [6]. In particular, nothing is known about stability of NHPI under oxidation of cyclohexene. Thus, the present study was aimed to understand the details of the catalytic action of NHPI in cyclohexene to CHHP oxidation, establish the mechanism of the catalyst deactivation, and recommend conditions for its better stability.

* Corresponding author.

E-mail address: kuznina@catcom.ru (N.I. Kuznetsova).

2. Experimental

2.1. Oxidation experiments

Oxidation of cyclohexene in acetonitrile solution of NHPI was performed at 1 bar of O₂ in a glass reactor (V 20 mL, 2.5 mL of solution), or at variable pressures of air in titanium reactor (V 300 mL, 50 mL of solution). For convenience, all data were normalized to 2.5 mL of the reaction solution.

2.2. Analysis of the reaction solution

Cyclohexene and oxidation products were analyzed by GC and GCMS after treatment of the solution with triphenylphosphine (see Supporting Information). O₂²⁻ groups in the products were additionally determined by iodometric titration. Quantitative analysis of NHPI was made by HPLC. Transformation of NHPI in the reaction solution was investigated by ¹H, ¹³C and ¹⁵N NMR.

The experimental technique is detailed in Supplementary material.

3. Results and discussion

3.1. Products of cyclohexene oxidation

Typical time dependencies of oxygen consumption during cyclohexene oxidation in a glass reactor (curves 1 and 2) and in titanium reactor (curve 3) are presented in Fig. 1. The curves 1 and 2 showed an induction period that was shorter in case of addition of a small amount of CHHP initiator. When the oxidation was conducted in the titanium reactor (curve 3), it was difficult to follow initial oxygen consumption because the reactor was heated to the reaction temperature for approximately 10 min. Most likely, the induction period was short or absent due to possible initiation of the radical Reaction (1) on metal parts of the reactor.

Table 1 shows the results of cyclohexene oxidation. In Runs 1, 2 and 3, conversion of cyclohexene for 7–8 h was in the range of 29–31%. The reductive treatment of the reaction solution with Ph₃P converted the main oxidation product CHHP to 2-cyclohexen-1-ol. After the treatment, GC determined 2-cyclohexen-1-ol corresponded to CHHP yield of 18, 26 and 20% in Runs 1, 2, 3, respectively. In addition, 2-cyclohexen-1-one (2.4%), cyclohexene oxide (0.2%), 2-cyclohexene-1,4-diols (0.3%, cis- and trans-), 1,4- and 1,2-cyclohexanediols (0.4%) were detected by GC in the reaction solution treated with Ph₃P. Dialcohols

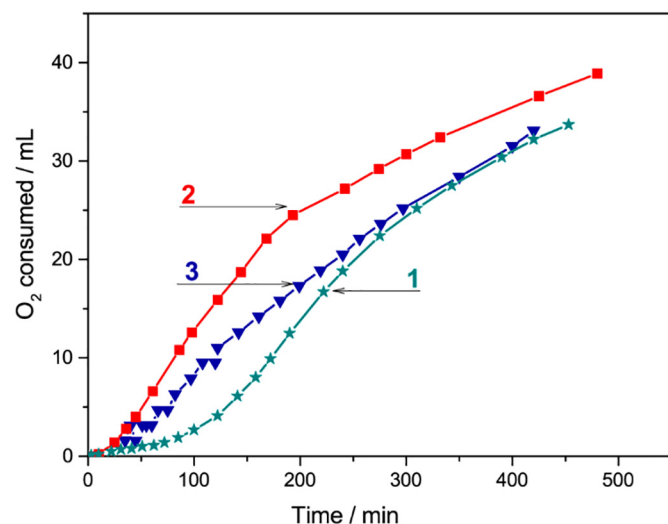


Fig. 1. Gas consumption versus time. Numbers near the curves correspond to runs in Table 1: O₂ 1 bar (1, 2) or 4.6 bar (3), addition of CHHP 50 μmol for (2).

appeared as the products of reduction of cyclohexane dihydroperoxide and 2-cyclohexene dihydroperoxide. In most oxidation experiments, iodometric titration gave slightly more O₂²⁻ groups than combined amount of hydroxyls in 2-cyclohexen-1-ol and other hydroxyl compounds determined by GC after the treatment of the reaction solutions with Ph₃P. This small excess could be attributed to dimer and polymer peroxides [18] which were converted by Ph₃P to hardly detectable high-boiling compounds. Thus, at the conversion of cyclohexene around 30%, CHHP was obtained with selectivity of 89% (Run 2 in Table 1). These conversion/selectivity parameters are comparable with those achieved in synthesis of other hydroperoxides. For instance, the NHPI catalyzed oxidation of hydrocarbons gave selectivity in the range of 90–96% at a conversion of 22–35% for alkylbenzenes (sec-butylbenzene, cyclohexylbenzene, cumene) [14, 15], and 40% selectivity at 16% conversion in case of isobutane [23].

3.2. Transformation of the NHPI catalyst

HPLC analysis of the reaction solutions showed that 15 to 60% of the initial amount of NHPI was lost for the reaction time (Table 1), probably, due to transformation into inactive species during catalysis. The gradual degradation of the catalyst caused slowing down in time of the oxygen consumption, as shown by the curves in Fig. 1. (The time-varying concentration of cyclohexene and oxidation products in the reaction solution could also contribute to the slowing of the reaction [6, 16].) The increase of initial NHPI resulted in an increase of cyclohexene conversion (from 12 to 31%) and yield of CHHP (from 10 to 26%, No 2 and 4–8 in Table 1). Amount of NHPI transformed during the reaction was the greater, the larger was initial NHPI, and the transformation decreased with a decrease in cyclohexene loading from 4.5 to 2.4 mmol and oxygen partial pressure from 1 to 0.5 bar (Fig. 2).

To follow the catalytic reaction and transformation of the catalyst in time, we performed the oxidation in more severe than usual conditions using higher temperature and oxygen pressure (Runs 10, 11 in Table 1). Intensive oxygen consumption began immediately as soon as the reactor was heated to 70 °C, whereas after 2.5 h a gradual deceleration of the oxidation process became remarkable (Fig. 3, curves 10, 11). HPLC analysis of NHPI showed that the rapid oxygen consumption for oxidation of cyclohexene within the first two hours was accompanied by intensive loss of NHPI (Fig. 3, curve NHPI). During this period, 40% of NHPI disappeared, and then the degradation continued slowly.

3.3. NMR study of the NHPI transformation

Deactivation of NHPI in homogeneous reactions is sometimes associated with hydrolysis to form phthalic acid. However, we did not observe formation of a precipitate of poorly soluble in CH₃CN phthalic acid. No phthalic acid was also detected in the reaction solution by NMR. Another transformation responsible for deactivation of NHPI could be recombination of the reactive PINO radicals to inactive dimers and trimers [8], or irreversible binding of the PINO radicals by any radical acceptor. The experimentally observed correlation of NHPI degradation not only with initial NHPI, but also with oxygen and cyclohexene concentrations (Fig. 2) indicated both oxygen and cyclohexene to be involved in deactivation of NHPI. In attempt to understand a nature of this phenomenon, we considered all possible interactions of NHPI and olefins other than allylic oxidation. In the presence of strong oxidants, NHPI formed PINO that reacted with olefins and cycloolefins by abstraction of an allylic H-atom. In the absence of molecular oxygen, the allyl radical attached another PINO radical to form monosubstituted allylic products [24, 25]. Addition of two PINO moieties across double bond of the olefins occurred under non-radical interaction assisted by Pb(IV). Due to anaerobic conditions, allylic oxidation was excluded in both cases.

Another type of interaction represented by radical addition of tert-RO• and ROO• to the double bond [26] was also realized by PINO

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