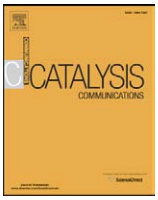
Catalysis Communications 12 (2010) 5–8

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom



Liquid-phase oxidation of p-xylene using N-hydroxyimides

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 12 July 2010
Accepted 13 July 2010
Available online 1 September 2010

Keywords:
p-Xylene
Terephthalic acid
Oxidation
Homogeneous catalysis
Organocatalysis

ABSTRACT

In this communication, we describe p-xylene oxidation with molecular oxygen at 373 K and atmospheric pressure using N-hydroxyimide catalysts. p-Xylene conversion was rather high over the first 2 h of reaction and complete by the end of the experiment. The product distribution curves versus reaction time are typical of consecutive reactions. The main intermediate product is p-toluic acid. Peak concentration and the shape of its concentration profile depend heavily on the N-hydroxyimide catalyst used. This effect seems to be related to the NO–H bond dissociation energy (BDE) of the N-hydroxyimides employed.

1. Introduction

Autoxidation reactions are becoming increasingly important in industrial oxidation processes for several reasons: they involve the most abundant and cheapest oxidizing reagent (molecular oxygen), and they usually require only mild temperatures and pressures. The use of molecular oxygen as an oxidant prevents the generation of pollutants, as occurs with stoichiometric oxidants. Molecular oxygen is a very convenient and potent oxidant, but its direct use is restricted by the spin conservation due to the triplet ground structure. Hydrocarbon autoxidations therefore occur via a free radical chain mechanism that hinders the control of selectivity [1].

Terephthalic acid (TPA) is the main raw material for polyester synthesis. It is produced by the liquid-phase catalytic oxidation of p-xylene (PX). Several processes have been developed for the oxidation of PX in liquid-phase, but about 70% of the terephthalate feedstock used worldwide is produced with a catalyst system discovered by Scientific Design (usually called the Amoco process), and almost 100% of new plants use this process [2]. Typically, PX is oxidized using acetic acid as solvent, one or two multivalent metal salts (mainly Co or Mn), and bromine as source of free radicals. The reaction temperature ranges from 160 to 200 °C, air is used as the oxygen source and the pressure is 1–2 MPa [2]. This reaction involves several intermediates: p-tolualdehyde (TALD), p-toluic acid (p-TOA), and 4-carboxybenzaldehyde (4-CBA), as shown in Fig. 1.

N-Hydroxyphthalimide (NHPI) promotes the oxidation of a variety of hydrocarbons with dioxygen in the presence or absence of transition metal salts [1,3–5]. In this oxidation, the phthalimide N-oxyl radical (PINO) generated in situ from the NHPI and dioxygen abstracts the hydrogen atom from the hydrocarbon to form an alkyl radical, which is readily trapped by dioxygen, affording oxygenated compounds. NHPI is a cheap, nontoxic catalyst that is easily prepared by the reaction of phthalic anhydride and hydroxylamine. It acts as a precursor of the phthalimido-*N*-oxyl (PINO) radical, which is the effective abstracting species in all of the free radical processes mediated by this N-hydroxy derivative. NHPI is thought to catalyze oxidation through the initial generation of the PINO radical by abstracting the hydrogen in NHPI. The PINO radical then abstracts the H-atom from the hydrocarbon to form an alkyl radical, which is readily trapped by dioxygen and then forms oxygenated compounds [6,7]. For NHPI to act as an efficient oxidation catalyst, it requires an O–H bond of similar strength so that the abstraction of H from the hydrocarbons is either exothermic or close to thermoneutral. However, it is also important for the O–H bond in NHPI to be weak enough so that PINO regeneration by the capping of no target alkyl radicals and peroxy radicals (ROO•) is also, ideally, exothermic [6]. The catalytic effect of NHPI on free radical autoxidations has two origins: a higher rate of propagation and, more importantly, a lower rate of termination owing to the extremely efficient scavenging of alkylperoxy radicals by NHPI [4].

Ishii et al. [3,8] subsequently showed that the combination of NHPI with a metal of variable valence (which is often referred to as the Ishii system), notably cobalt, affords an effective catalytic system for the autoxidation of a broad range of organic substrates, e.g.: alkanes [9,10] and alkylaromatics [11]. The combination of NHPI with Co/Mn salts was shown to catalyze this oxidation under milder conditions (100 °C and

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doi:10.1016/j.catcom.2010.07.010

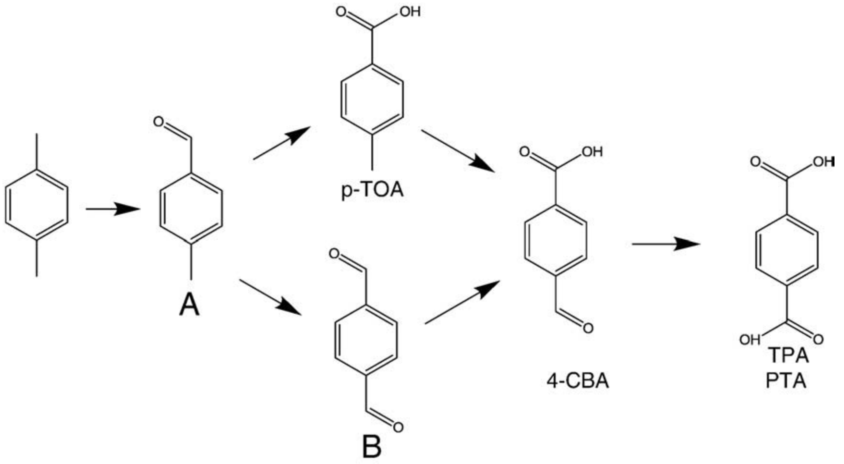

Fig. 1. Reaction scheme for liquid-phase p-xylene oxidation.

1 bar) [6]. Once the NHPI has been recognized as a valuable catalyst for the aerobic oxidation of a wide range of organic compounds under mild conditions, a major focus of interest is the search for alternative catalysts with a similar structure [12,13].

According to the state of the art, this work was undertaken to further knowledge on the autoxidation of alkylaromatics to other N-hydroxyimides with a homogeneous catalyst such as NHPI. In our current research, several commercial N-hydroxyimides have been tested as catalysts and screened in the oxidation reaction of p-xylene with dioxygen under mild conditions.

2. Experimental

2.1. Reagents

All the reagents used here were commercially available: p-xylene, acetic acid, N-hydroxyphthalimide (NHPI), N-hydroxysuccinimide (NHSI) and N-hydroxymaleimide (NHMI), were purchased from Sigma-Aldrich; N-hydroxy-1,8-naphthalimide (NHNI) from Alfa Aesar and carbonic acid tert-butyl phthalimido ester (CATPE) from TCI Europe N.V. All compounds were used as received without further purification.

2.2. p-Xylene oxidation reaction

The oxidation of p-xylene was performed in a glass batch reactor equipped with a magnetic stirrer and a septum for withdrawing samples at intervals of 1 h. The system was also equipped with a condenser in order to ensure complete condensation and recycling of the evaporated compounds. In a typical run, 5 mL (40 mmol) of p-xylene, 8 mmol of hydroxyimide, 0.2 mmol of $Co(OAc)_2$, 0.2 mmol of $Mn(OAc)_2$ and 100 mL of glacial acetic acid (HOAC) were mixed together in a stirred glass reactor, which was then purged with nitrogen. Stirring speed was set at 1500 rpm. After reaching the desired temperature (100 °C) pure oxygen was introduced into the reactor. At the end of the reaction, the solid and mother liquor were separated for filtration. The recovered solid product was dried and weighed. The mother liquor containing the catalyst, oxidation intermediates and solvent were analyzed using a gas chromatograph fitted with a flame ionization detector (GC-FID) on an Agilent 6850 device equipped with an HP-WAX capillary column. p-Xylene conversion was defined as (moles of p-xylene reacted)/(moles of p-xylene fed to the reactor) × 100%.

3. Results and discussion

The oxidation of p-xylene was carried out in liquid-phase under mild reaction conditions (100 °C and atmospheric pressure) in the presence of N-hydroxyimide catalysts. p-Xylene oxidation to terephthalic acid is a typical example of consecutive reaction. As each p-xylene molecule incorporates 4 O-atoms to yield TPA, several reaction intermediates containing 1 to 3 O-atoms are expected. As outlined in Fig. 1, p-xylene is first oxidized to an aldehyde; this aldehyde is then oxidized into p-toluic acid (p-TOA), which is converted into 4-CBA prior to yielding TPA. A parallel route starting with p-tolualdehyde and ending with 4-CBA is expected, adjudging from the appearance of the two intermediates labeled A and B whose maxima were reached prior to the peak concentration of the 4-CBA product.

As a first approach, and in order to reveal the influence of the type of N-hydroxyimide on the performance for p-xylene oxidation, all concentrations were kept constant in all the experiments. The key parameter controlling the reactivity of these N-hydroxyimides is the bond dissociation energy (BDE) of the NO–H bond. Although certain discrepancies can be observed in the absolute BDE values of N-hydroxyimides reported in the literature, there is current agreement on their relative values whatever the source or calculation method used, solvent present or gas phase calculation performed. The generally accepted BDE order is NHNI > NHSI ≫ NHPI ~ NHMI (Table 1). When these BDE values are related to the catalytic effect,

Table 1
Bond dissociation energy (BDE) of NO–H for the N-hydroxyimides used in this study taken from reference [15].

N-hydroxyimide	BDE (kcal/mol)
NHPI	81.2
NHMI	81.2
NHSI	86.0
NHNI	87.6

Table 2
Results after 24 h of reaction in liquid-phase p-xylene oxidation with molecular oxygen. Reaction conditions: temperature = 373 K; pressure = 1 bar (O_2); N-hydroxyimide/p-xylene = 20 mol% Co/PX = Mn/PX = 0.5 mol%.

Products distribution (%)				
Catalyst	p-Xylene conversion (%)	p-TOA	4-CBA	TPA
Blank with only NHSI	45.0	87	6.0	8.0
Blank with only Co and Mn salts	0	0	0	0
NHPI	100.0	33.4	4.7	61.9
NHMI	13.0	0.0	0.0	0.0
CATPE	100.0	49.0	5.5	45.5
NHNI	100.0	12.1	3.2	84.6
NHSI	100.0	0.7	0.7	98.6

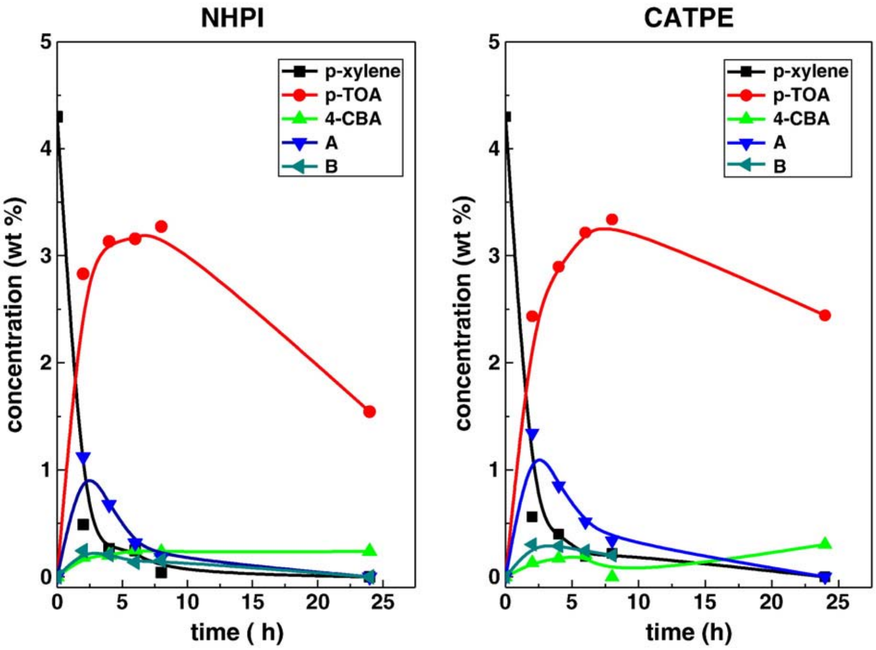

Fig. 2. Concentration profiles in liquid-phase p-xylene oxidation with molecular oxygen using NHPI (left panel) and CAPTE (right panel) as catalysts (reaction conditions: temperature = 373 K; pressure = 1 bar; NHPI/PX = CAPTE/PX = 20 mol% Co/PX = Mn/PX = 0.5 mol%).

the NO–H bond cleavage is responsible for radical formation in p-xylene oxidation.

Two blank experiments have been conducted in the absence of either N-hydroxyimides or Co and Mn in order to show the influence of each additive on the performance (Table 2). No reaction is observed in the absence of NHSI because no radical formation from cobalt or manganese occurs under the conditions selected in this work [3,5,14]. Reaction occurs to some extent in the absence of metallic salts, but the activity is lower than when these compounds are present. NHSI oxidizes p-xylene slowly, and the amount of final PTA is very low. This finding is consistent with previously reported reaction mechanisms [3,5], where N-hydroxyimides are responsible for radical formation and the cobalt and manganese are co-catalysts that enhance the activity of the N-hydroxyimides.

For the N-hydroxyimides selected, xylene conversion was complete by the end of the experiment, except for the NHMI, which did not record any activity in the target reaction. The changes in the concentration of p-xylene reactant and of reaction products as a function of reaction time are displayed in Figs. 2–4. p-Xylene is consumed at the beginning of the reaction. The p-xylene disappearance rate is high and similar for NHPI, NHSI and CATPE catalysts, whereas some retardation is observed at short reaction times when NHNI is employed. p-Xylene conversion is low for reaction times under 5 h, but after this point its consumption increases sharply, and no p-xylene is detected at reaction times over 6 h.

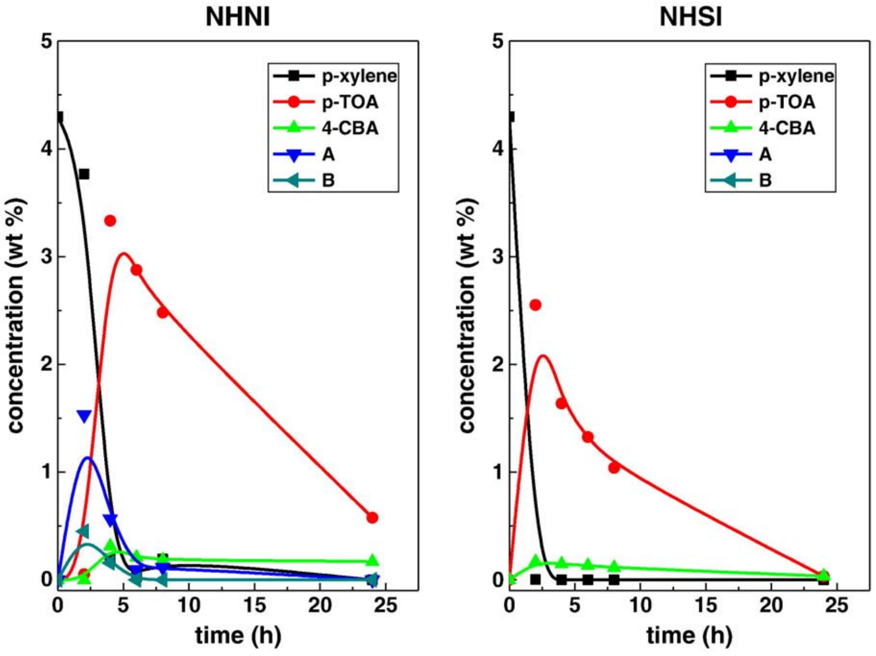

Fig. 3. Concentration profiles in liquid-phase p-xylene oxidation with molecular oxygen using NHNI (left panel) and NHSI (right panel) as catalysts (reaction conditions: temperature = 373 K; pressure = 1 bar; NHNI/PX = NHSI/PX = 20 mol% Co/PX = Mn/PX = 0.5 mol%).

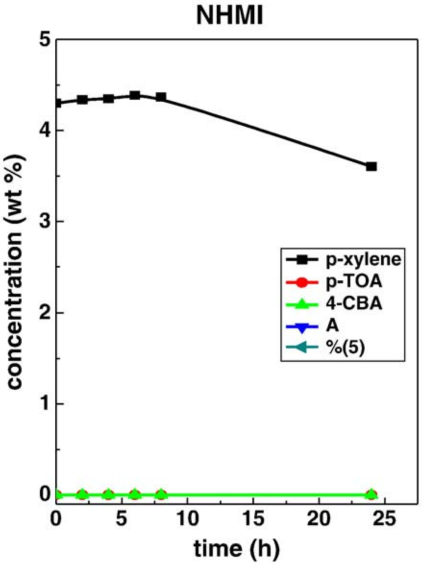

Fig. 4. Concentration profiles in liquid-phase p-xylene oxidation with oxygen using NHMI as homogeneous catalyst (reaction conditions: temperature = 373 K; pressure = 1 bar; NHMI/PX = 20 mol% Co/PX = Mn/PX = 0.5 mol%).

The odd behavior displayed by the NHNI can be related to the limited solubility of this compound in the reaction medium.

Consistent with the reaction pathways shown in Fig. 1, reactions conducted in the presence of NHPI, CAPTE and NHNI catalysts yield a maximum concentration of A intermediate precisely at reaction times shorter than that required for achieving the peak concentration of p-TOA. Furthermore, this A intermediate could not be detected at longer reaction times, indicating that its disappearance rate is much higher than in the other three N-hydroxyimides (NHPI, CAPTE and NHNI).

The main intermediate product is p-TOA (Figs. 2–4). The concentration profiles follow the typical behavior of an intermediate compound; first its concentration grows, it then peaks and subsequently decreases with time. The peak concentration and the shape of its profile depend heavily on the N-hydroxyimide catalyst used. Indeed, the disappearance rate of p-TOA, which equals the formation rate of TPA, follows the order: CAPTE < NHPI < NHNI < NHSI. This means that NHSI is the most effective catalyst for p-xylene oxidation, yielding TPA with a selectivity of 98.6% at the maximum reaction time (24 h) explored. The most difficult reaction step is related to the oxidation of p-TOA; its disappearance rate, therefore, is related to the catalytic activity of the N-hydroxyimide used in p-xylene oxidation. It is well known that the catalytic activity of N-hydroxyimides in radical reactions can be related to the BDE of NO–H [4] which follows the order: NHNI > NHSI ≫ NHPI > NHMI (Table 1). The catalytic activity order of N-hydroxyimides is very similar to the BDE order, but is lower than expected for NHNI due to its limited solubility. The importance of the BDE value is related to the reaction mechanism, where the stability of the corresponding nitroxyl radical towards decomposition is essential [3,4,6].

4. Conclusions

From both the approach and results obtained in this work, the following conclusions can be drawn: (i) the liquid-phase oxidation of p-xylene with molecular oxygen to TPA has been efficiently performed under very mild reaction conditions (373 K and 1 bar) using different N-hydroxyimides (NHPI, NHMI, NHNI, NHSI, and CATPE) and Co and Mn salts as homogeneous catalysts; (ii) the time at which the peak concentration of p-TOA is reached and the slope of its decay at longer reaction times depend heavily on the N-hydroxyimide catalyst used; (iii) the catalytic activity of the tested N-hydroxyimides in the target reaction is related to the bond dissociation energy (BDE) of NO–H: NHNI > NHSI ≫ NHPI > NHMI; the only exception to this rule is NHNI, which appears to be due to its limited solubility in the liquid-phase under the conditions selected in this work.

Acknowledgement

We thank our research sponsor, The King Saud University, Riyadh (Saudi Arabia).

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