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Selective catalytic aerobic oxidation of substituted ethylbenzenes under mild conditions

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ABSTRACT

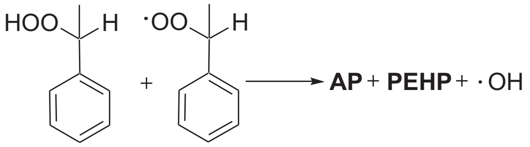
Ethylbenzene is oxidized to the corresponding hydroperoxide (PEHP) with high selectivity, under mild conditions, by means of a metal-free catalytic system consisting of an aldehyde and *N*-hydroxyphthalimide (NHPI). The process occurs via a free radical mechanism by *in situ* generation of the phthalimido-*N*-oxyl (PINO) radical. The protocol is applied with success on a wide range of substituted ethylbenzenes (ETBs). The competitive experiments carried out on few couples of ETBs revealed a marked polar effect, this proving the key role that PINO plays as real hydrogen abstracting species, at least at low conversion. At higher conversion, the formation of highly reactive $^{\bullet}$OH radicals from PEHP reduces the differences in the reactivity of selected couples of ETBs. The study of the reaction mechanism, including the investigation on aldehyde and catalyst percentage amounts, and temperature and concentration effects, allows to achieve the final PEHPs products with good yields.

1. Introduction

Aerobic oxidation of ethylbenzene (ETB) to the corresponding hydroperoxide (Scheme 1) is becoming increasingly important, due to the key role that phenyl ethyl hydroperoxide (PEHP) plays as industrial intermediate for the production of propylene oxide and styrene monomer (Shell SM/PO Process) [1].

The industrial autoxidation of ETB is carried out under metal-free conditions and at 130 °C, in order to promote the decomposition of tiny amounts of (PEHP), which may occur by a thermal homolytic cleavage of the O—O bond (Eq. (1a)) or by a bimolecular process according to Eq. (1b) [2]. PEHP acts in turn as radical chain initiator (Eqs. (2) and (3), Scheme 1).

Under these operative conditions, an increase of ETB conversion would be reflected into a decrease of selectivity into PEHP (Eq. (7)). For this reasons conversion is kept low (about 13%) to minimize by-products. The selectivity for ethylbenzene to PEHP is approximately 90%, and the selectivity to MPC and AP is 5–7% [3].



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In the last decades several efforts have been devoted to the development of new catalytic systems with the aim to increase the conversion of ETB and, at the same time, to provide the corresponding hydroperoxide with high selectivity. In 2005, Fierro and co-workers reported the beneficial effect of the addition of tiny amounts of alkaline and alkaline-earth metal oxides in the oxidative batch, in order to neutralize the acidic by-products of the reaction. As result, selectivity in PEHP increased, but conversion of ETB was lower than 10% [4].

In recent years, *N*-hydroxyphthalimide (NHPI) has been reported as an effective catalyst in many oxidative processes [5]. NHPI acts as a precursor of phthalimido-*N*-oxyl (PINO) radical, which is the real hydrogen abstracting species (Eq. (8)). Its activation may occur by means of transition metal salts [6–8], but the presence of metallic co-catalysts is detrimental when the final goal is to achieve hydroperoxides selectively.

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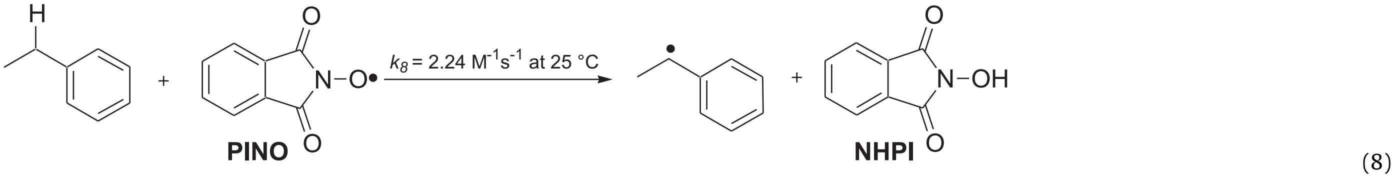

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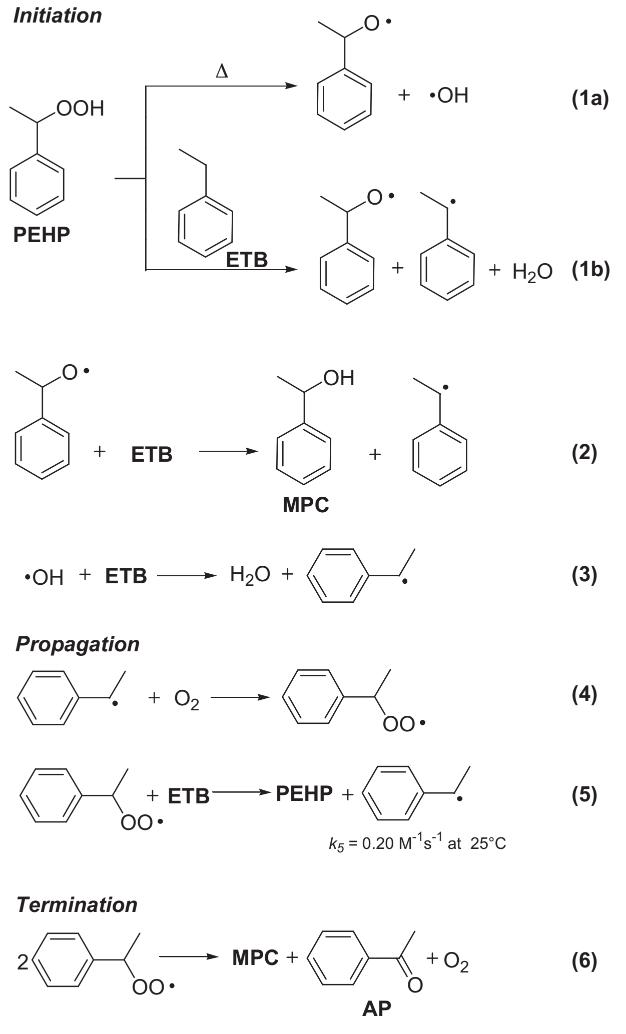
In 2003, we reported the metal-free nitric aerobic oxidation of ETB catalyzed by the I_2/NHPI system in acetic acid solution, achieving methyl phenyl carbinol (MPC) through the corresponding acetate in high yields as unique final product [9]. Several other transition metal-free initiators have been employed in combination with NHPI for the aerobic oxidation of hydrocarbons, including alkaline-earth chlorides [10], oximes [11], quinones [12], phenantrolines [13], xanthones [14], quaternary ammonium bromides [15] and nitriles [16]. Nevertheless, when employed for the catalytic oxidation of ETB, all these systems afforded almost quantitatively the corresponding acetophenone (AP).

In 2009, Fierro and co-workers significantly improved their aforementioned approach by performing the oxidation of ETB to PEHP in the presence of NHPI and ppm amounts of NaOH [17], reaching a higher selectivity in PEHP (ca. 80% mol) with a substrate conversion up to 15%. However, under the reported operating conditions (~150 °C) the organocatalyst undergoes fast decomposition, this limiting the interest for this approach from an industrial point of view.



Scheme 1. Autoxidation mechanism for ETB.

On the bases of our preliminary studies on the aerobic epoxidation of primary olefins by means of an NHPI/aldehyde system [18], we have recently reported that cumene (CU) can be selectively converted to the corresponding hydroperoxide via a free-radical chain promoted by NHPI and initiated by small amounts of aldehydes [19]. Peroxidation of secondary alkylaromatics shows two main drawbacks if compared with the analogous reaction on CU: (i) the secondary C—H benzylic bond of ETB is less reactive than the tertiary C—H benzylic bond of CU; (ii) PEHP product, which has a tertiary C—H benzylic bond more reactive than the secondary one of the starting ETB, can further react affording secondary products [2].

In 1997, Einhorn and co-workers conducted a series of aerobic oxidations on a wide range of hydrocarbons, combining stoichiometric amounts of acetaldehyde (MeCHO) with catalytic quantities of NHPI [20]. Among the organic substrates, they considered the oxidation of ETB, obtaining MPC and AP as unique products, while EBTH was not observed.

In the present work, which follows a patent application [21], we exploit the key role that the NHPI/MeCHO system plays in the autoxidation of ETB and analogous secondary alkylaromatics to afford the corresponding hydroperoxides in good yields and high selectivity, under mild conditions.

2. Experimental

2.1. Materials

All starting materials and catalysts were purchased from commercial suppliers without further purification with the exception of **1d**, which was prepared from the corresponding *p*-methoxy acetophenone by reduction with N_2H_4, according to the procedure reported in the literature [22].

2.2. General procedure

5 mmol of **1a**–**f** and the desired amounts of MeCHO and NHPI were added to 10 mL of acetonitrile in a 50 mL double-neck round-bottom flask. The solution was maintained for 6 h under an atmospheric pressure of O_2 and at the temperature of choice, with magnetic stirring. The oxidation products **2a**, **3a**–**f** and **4a**–**f** were identified by comparison with authentic samples commercially available. The hydroperoxides **2b** [23], **2c**, **2d** [23], **2e** [24] and **2f** [24] were isolated by flash chromatography (40–63 μm silica gel packing; hexane/ethyl acetate, 9/1), characterized by H NMR and compared with analytical data reported in literature. Complete characterization of **2c** is reported below. Conversions and yields were determined by HPLC analysis (reverse phase column; MeCN/MeOH/H_2O, 35/5/60), with cumyl alcohol added as internal standard, and confirmed by 1H NMR.

4-(1-Hydroperoxyethyl)benzonitrile (**2c**): ^{1}H NMR ($CDCl_3$) δ (ppm): 1.46 (d, 3H, CH3, *J* = 6.82 Hz); 2.16 (s, 1H, OOH); 5.11 (q, 3H, CH2, *J* = 6.82 Hz); 7.48 (d, 2CH Ar, *J* = 8.12 Hz); 7.67 (d, 2CH Ar, *J* = 8.12 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.5, 76.3, 105.2, 112.0, 120.5, 125.8, 140.8. ESI-MS (*m*/*z*): 186 (100), 102.2 (0.045).