



## 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  $\cdot\text{OH}$  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.

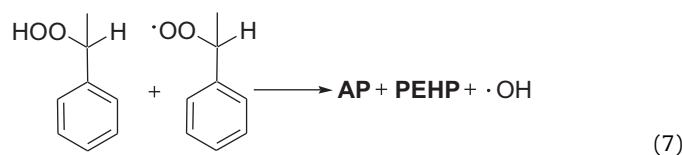
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### 1. Introduction

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).

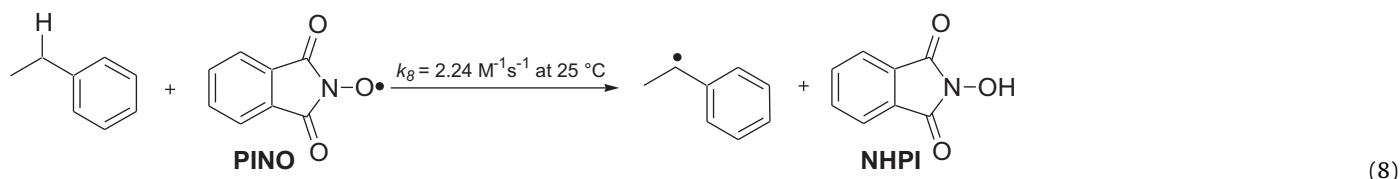
Under these operative conditions, an increase of ETB conversion would be reflected into a decrease of selectivity into PEHP (Eq. (7)). For this reasons conversion is kept low (about 13%) to minimize by-products. The selectivity for ethylbenzene to PEHP is approximately 90%, and the selectivity to MPC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



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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In 2003, we reported the metal-free nitric aerobic oxidation of ETB catalyzed by the  $\text{I}_2/\text{NHPI}$  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], xanthenes [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 ( $\sim 150^\circ\text{C}$ ) the organocatalyst undergoes fast decomposition, this limiting the interest for this approach from an industrial point of view.

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

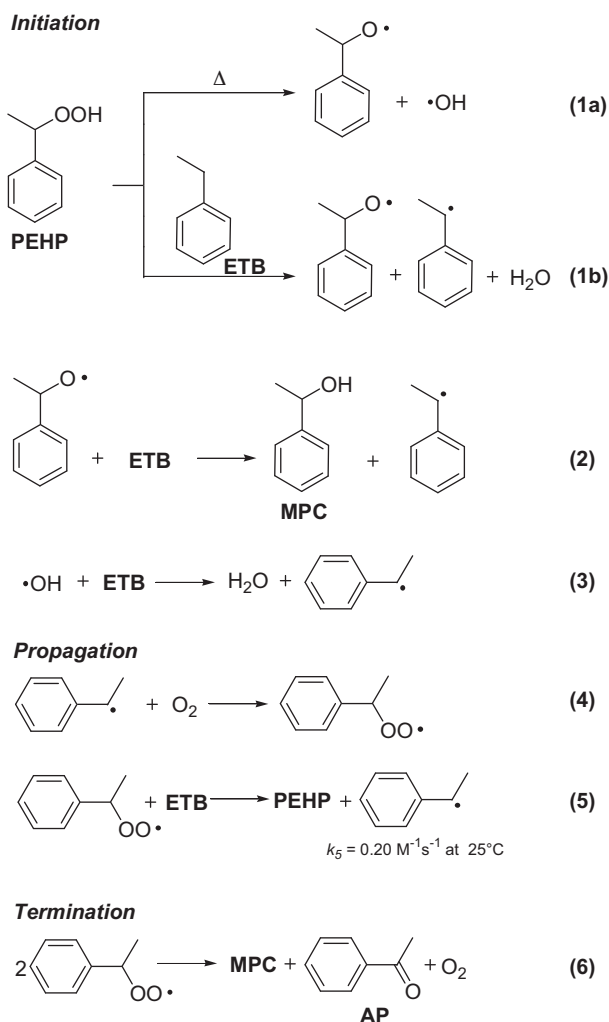
### 2.1. Materials

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  $\text{N}_2\text{H}_4$ , 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  $\text{O}_2$  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  $\mu\text{m}$  silica gel packing; hexane/ethyl acetate, 9/1), characterized by  $^1\text{H}$  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/ $\text{H}_2\text{O}$ , 35/5/60), with cumyl alcohol added as internal standard, and confirmed by  $^1\text{H}$  NMR.

**4-(1-Hydroperoxyethyl)benzotrile (2c)**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.46 (d, 3H, CH<sub>3</sub>,  $J = 6.82$  Hz); 2.16 (s, 1H, OOH); 5.11 (q, 3H, CH<sub>2</sub>,  $J = 6.82$  Hz); 7.48 (d, 2CH Ar,  $J = 8.12$  Hz); 7.67 (d, 2CH Ar,  $J = 8.12$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (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).



Scheme 1. Autoxidation mechanism for ETB.

### 2.3. General procedures for determining the relative and absolute rate constants of the aerobic oxidations of substituted **1a–f**

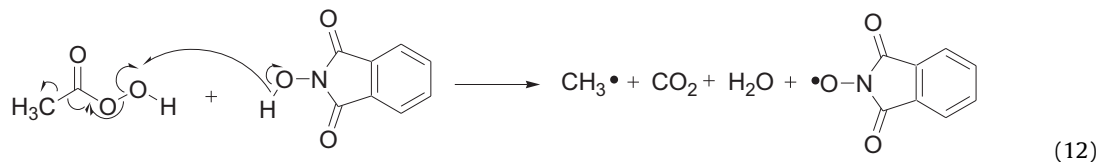
Competitive experiments were run between **1a** (2.5 mmol) and substituted ethylbenzenes **1b–f** (2.5 mmol), and a suitable reaction time (2 h) was utilized to have low conversions of ETBs to the corresponding hydroperoxides. The conversions were determined by GC, using cumyl alcohol as internal standard, and the response factors were measured by employing authentic samples. Yields were determined as described before. These competitive kinetics were utilized to determine the relative rate constants of the aerobic oxidations of **1b–f** to **2b–f**, reported in Table 3. The relative rate constants were evaluated using Eq. (9), since the absolute rate constant for the hydrogen atom abstraction from ETB **1a** by PINO radical, which is the rate-determining step of the oxidative process, had been already evaluated by Lucarini et al. [25] by means of EPR technique.

$$\frac{k_x}{k_H} = \frac{\log((1b-f)_0 - [2b-f])/[1b-f]_0)}{\log((1a)_0 - [2a])/[1a]_0)} \quad (9)$$

## 3. Results and discussion

### 3.1. Effect of initiator

Our initial experiments were conducted with the aim of reproducing Einhorn's conditions, that is by operating in the presence

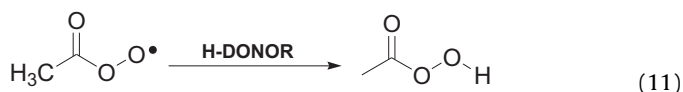
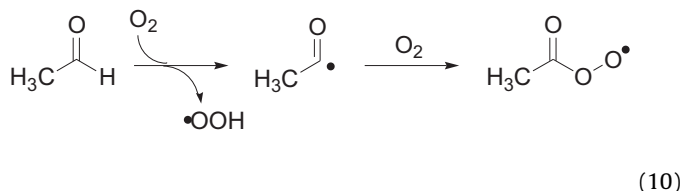


of stoichiometric amounts of MeCHO. However, as verified for the oxidation of cumene [19], also in this case we observed a completely different behavior with respect to Einhorn's reported data. In fact, PEHP resulted the primary product, while small amounts of MPC were observed, being AP the major by-product (Table 1, entry 1).

Even more interesting, by decreasing the amount of MeCHO, the conversion also decreased, but the selectivity in PEHP increased up to 90% (Table 1, entries 2–6). This behavior follows the trend of the traditional process, but our results showed that tiny amounts

of MeCHO were sufficient to perform the desired product even at room temperature and atmospheric pressure. However, the presence of MeCHO was essential to initiate the free-radical chain (entry 7).

Under these very mild conditions, the initiation phase occurs in a three-step process. In the presence of O<sub>2</sub>, acetaldehyde is oxidized to the corresponding acyl peroxy radical (Eq. (10)), which in turn may abstract a hydrogen atom from ETB, NHPI, another molecule of MeCHO, but also from PEHP and MPC, forming the corresponding peracetic acid (Eq. (11)). In all of the cases the hydrogen abstraction by acyl peroxy radical occurs faster than by an alkyl peroxy radical. Peracetic acid may be in turn involved in the generation of PINO from NHPI, through a molecule-induced homolysis process (Eq. (12)).



### 3.2. Effect of catalyst

The key role of NHPI catalysis was evident. In fact, in the absence of the organocatalyst no reaction occurred under our mild operating conditions, while an increase in NHPI concentration led to higher conversions, with still high selectivity in PEHP (Fig. 1).

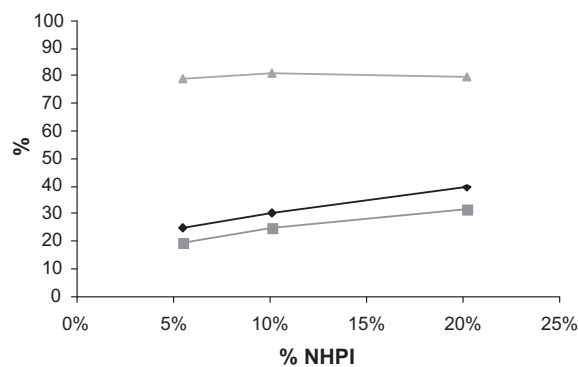
NHPI is crucial in reducing the concentration of all the fast terminating oxygen centered radical species deriving from the autoxidation of both MeCHO and ETB. This role was outlined by the

**Table 1**  
Effect of the amount of MeCHO for the aerobic oxidation of ETB.<sup>a</sup>

Run	MeCHO (%)	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>		
			PEHP	MPC	AP
1	100	36	57	6	37
2	90	31	65	12	23
3	45	29	70	3	27
4	10	26	82	–	18
5	5	21	90	–	10
6	2.5	13	92	–	8
7	–	–	–	–	–

<sup>a</sup> 5 mmol of ETB in 10 mL of CH<sub>3</sub>CN were stirred for 6 h at 25 °C and atmospheric pressure of O<sub>2</sub> in the presence of NHPI (10% mol) and MeCHO (as reported in the table) in a percent amount with respect to ETB.

<sup>b</sup> Conversions and selectivity of the known reaction products were determined by HPLC with cumyl alcohol added as internal standard and confirmed by <sup>1</sup>H NMR.

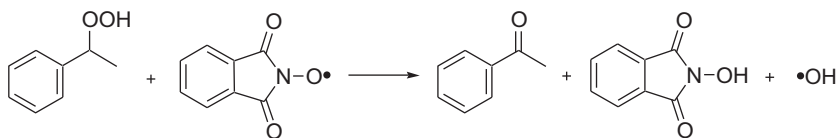
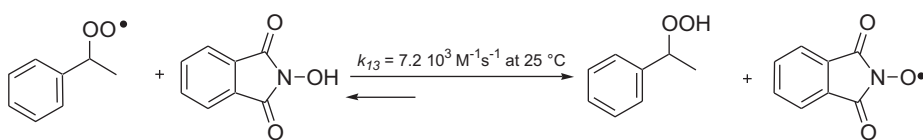


**Fig. 1.** ETB conversion (◆) and yield (■) and selectivity (▲) in PEHP versus percent amount of NHPI. See Table 1, note (a) for reaction conditions.

experimental results of Table 1. MPC, which under our operating conditions can only derive by the Russell type termination process (Eq. (6)), was generally not observed in the presence of NHPI. Only with higher quantities of MeCHO tiny amounts of alcohol were detected, probably due to the presence of a higher concentration of fast terminating radical species deriving from MeCHO.

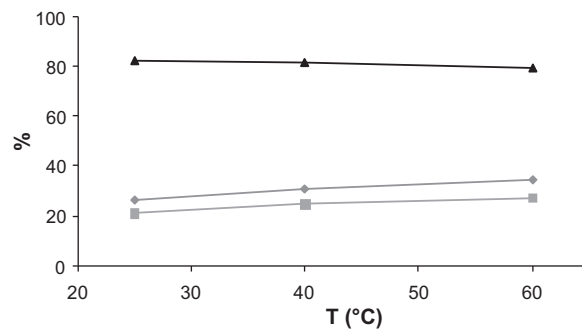
In the catalyzed propagation phase, PINO radical can promote the hydrogen abstraction from ETB, forming the corresponding  $\alpha$ -methyl benzyl radical (Eq. (8)). By comparing  $k_5$  with  $k_8$  we conclude that Eq. (8) occurs 11 times faster than Eq. (5), this demonstrating the catalytic role of NHPI.  $\alpha$ -Methyl benzyl radical in turn can be trapped by molecular oxygen according to Eq. (4). Once formed, the peroxy radical can undergo Russell termination (Eq. (7)) or promote the hydrogen abstraction from NHPI (Eq. (13)) or another molecule of ETB (Eq. (5)), present in large excess. If we consider the ratio between  $k_{13}$  and  $k_5$  ( $\sim 36,000$ ), we can conclude that NHPI behaves as an ideal H-donor even at very low concentrations, trapping peroxy radicals. In this way the Russell termination is inhibited and the selectivity in PEHP is increased. Thus the presence of NHPI favorably affects the kinetics of the process by decreasing the rate of the termination steps [26] and by increasing the rate of the propagation steps.

The formation of AP as main by-product should be ascribed to the fast hydrogen abstraction from PEHP by means of peroxy radical (Eq. (7)) or of PINO itself (Eq. (14)).



### 3.3. Effect of temperature

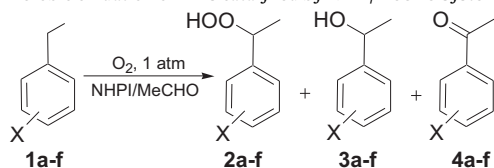
On the contrary of what observed for cumene [19], an increase of the reaction temperature led just to a poor improvement of the process efficiency in terms of conversion and yield (Fig. 2). This behavior should be ascribed to the slightly higher bond dissociation energy (BDE) of the secondary C–H bond for ETB (85.4 kcal/mol) [27] with respect to the BDE of tertiary C–H bond of CU (84.4 kcal/mol) [28]. This difference determines an activation energy ( $E_a$ ) for the reaction of hydrogen abstraction by PINO



**Fig. 2.** ETB conversion (◆) and yield (■) and selectivity (▲) in PEHP versus  $T$  (°C). See Table 1, note (a) for reaction conditions.

**Table 2**

Aerobic oxidation of ETBs catalyzed by NHPI/MeCHO system.<sup>a</sup>



1	X	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>		
			2	3	4
1a	H	31	2a: 81	–	4a: 19
1b	<i>p</i> -Cl	33	2b: 84	–	4b: 16
1c	<i>p</i> -CN	21	2c: 74	–	4c: 26
1d	<i>p</i> -OCH <sub>3</sub>	42	2d: 91	–	4d: 9
1e	<i>p</i> -CH <sub>3</sub>	36	2e: 82	–	4e: 18
1f	<i>m</i> -CH <sub>3</sub>	25	2f: 82	–	4f: 18

<sup>a</sup> See Table 1, note (a).  $T = 40^\circ\text{C}$ . MeCHO 10%.

<sup>b</sup> See Table 1, note (b).

higher for ETB than for CU. As a consequence, for the restricted range of temperatures here investigated, conversion moved from 26% at  $25^\circ\text{C}$  to just 34% at  $60^\circ\text{C}$ . Nevertheless, by operating at temperatures higher than  $60^\circ\text{C}$ , thermal decomposition of PEHP may occur, this limiting the selectivity of the process.

### 3.4. Effect of substituents

With the optimized conditions in hand, we set out to examine the scope of the reaction for a wider range of substituted ethylbenzenes (ETBs). The results reported in Table 2 clearly confirm the general applicability of the process for a wide range of secondary alkyl aromatics.

Moreover, in order to investigate the polar effect of substituents on the aromatic ring and to verify the role of PINO as principal

**Table 3**  
Absolute rate constants for the H-atom abstraction from ETBs by PINO radical at 25 °C.

X	$k$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_X/k_H$
H	2.24 <sup>a</sup>	1.00
<i>p</i> -Cl	0.16	0.072
<i>p</i> -CN	0.06	0.022
<i>p</i> -OCH <sub>3</sub>	11.05	4.93
<i>p</i> -CH <sub>3</sub>	2.76	1.23
<i>m</i> -CH <sub>3</sub>	2.11	0.94

<sup>a</sup> From Ref. [25].

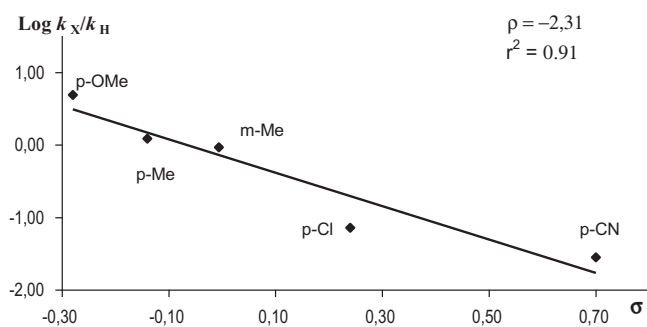
hydrogen abstracting specie, we have determined the absolute rate constants by competitive kinetics at shorter reaction times (2 h). The results are reported in Table 3, while Fig. 3 displays a Hammett correlation between the results presented in the table and values of  $\sigma$ .

For all the substituents reported in Table 3, the effects on the values of the BDE of their benzylic C–H bonds is rather poor and the polar effect largely prevails over the enthalpic effect, which leads to a satisfactory Hammett correlation.

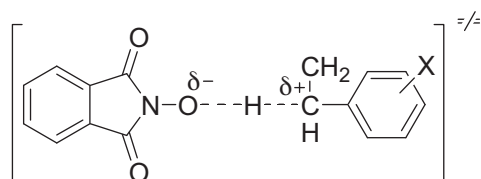
The key role of polar effects in the presence of NHPI was already reported for both the aerobic oxidation of substituted benzylic alcohols [29,30] and the aerobic oxidation of 1-(4-methoxyphenyl)ethanol by means of NHPI aryl substituents [30].

The observed behavior has to be related to a more-pronounced electrophilic character of the PINO radical relative to the peroxy radical, which induce a stabilization of the transition state of Eq. (8) (Fig. 4).

At longer reaction times (6 h) the difference in the reactivity of selected couple of substituted ethylbenzenes decreases. This behavior could be ascribed to the higher conversion, which favors Eqs. (7) and (14), leading to the formation of hydroxyl radicals. The latter are very reactive, owing to the strong O–H bond formed in the final H<sub>2</sub>O product, and are not able to discriminate between the two ETBs in the hydrogen abstraction process, the enthalpic effect being predominant under these conditions.



**Fig. 3.** Hammett correlation for aerobic oxidation of substituted ethylbenzenes. See Table 3 for reaction conditions. Reaction time: 2 h.



**Fig. 4.** Transition state for Eq. (8).

**Table 4**  
Aerobic oxidation of ETB in CH<sub>3</sub>CN at different concentrations catalyzed by NHPI/MeCHO system.<sup>a</sup>

Run	CH <sub>3</sub> CN (mL)	T (°C)	NHPI (%)	PEHP <sup>b</sup>	
				Y (%)	S (%)
1	10	40	2	12.0	89
2	10	40	5 <sup>c</sup>	14.3	90
3	10	70	2	10.8	89
4	10	70	5	15.9	93
5	10	70	10 <sup>c</sup>	19.5	89
6	5	40	2	12.8	91
7	5	40	5 <sup>c</sup>	12.5	92
8	5	70	2	13.4	91
9	5	70	5 <sup>c</sup>	13.5	93
10 <sup>d</sup>	2	70	1	28.3	84

<sup>a</sup> 42 mmol of ETB in 10 mL of CH<sub>3</sub>CN were stirred for 6 h at atmospheric pressure of O<sub>2</sub> in the presence of NHPI and MeCHO (2% with respect to ETB).

<sup>b</sup> See Table 1, note (b).

<sup>c</sup> Reaction medium non homogeneous.

<sup>d</sup> 36 mmol of cumene were employed instead of ETB.

### 3.5. Effect of ETB concentration

Autoxidation of alkylaromatics is usually conducted in the absence of co-solvents. However, due to its polar nature, NHPI has a low solubility in alkylbenzenes at the mild temperature employed in our protocol. Thus, the use of polar solvents such as acetonitrile or acetone is mandatory in order to dissolve the quantities of NHPI necessary for observing a good catalytic activity. This aspect could represent the main limit of the oxidative process here proposed, if the volumes of solvent were significantly higher than those of the starting material. For this reason we wanted to investigate the effect of ETB concentration in order to identify the best operating conditions.

As shown in Table 4 (entries 1 and 2), in a first step we increased the amount of ETB up to 42 mmol (~5 mL), by maintaining the same volume of acetonitrile (10 mL), with 2% of MeCHO. At 40 °C, only with 2% of NHPI the reaction medium resulted homogeneous. An increase of temperature had the unique benefit of increasing the solubility of the catalyst (entries 3–5), reaching a final yield of about 20%, while selectivity was maintained around 90%. We then further increased the concentration of ETB by decreasing the amount of co-solvent with a final 1/1 volume ratio between ETB and CH<sub>3</sub>CN. The reaction appeared competitive with the classical procedure, achieving a 13% yield in PEHP with high selectivity. In this case, an increase of temperature did not provide significant benefits in terms of final yields, this demonstrating that the 2% of catalyst is the higher concentration of NHPI reachable under these very mild conditions.

Optimized conditions were also found for the aerobic oxidation of cumene (CU) (entry 10). As expected for this more reactive substrate, yields in the corresponding hydroperoxide (CHP) were higher, even with just 1% of NHPI and a final volume ratio between CU and CH<sub>3</sub>CN of 5/2.

NHPI, which remains unchanged during the reaction due to the low temperature, could be easily recovered at the end of the oxidation by crystallization from the reaction mixture, after removing the polar solvent by distillation.

## 4. Conclusion

We have demonstrated that the NHPI/MeCHO catalytic system, recently reported for the aerobic oxidation of tertiary alkylaromatics, is also efficient in the peroxidation of the less reactive secondary ones. The corresponding hydroperoxides are achieved in good yields and high selectivity. The protocol of the reaction, optimized for the autoxidation of ETB, has been proved to be suitable



for a wider range of ethylbenzenes. The polar effect emphasized by the Hammett correlation clearly shows the key role played by the PINO radical in the propagation phase of the radical chain. Moreover, the possibility to operate at very high concentration of ETB in polar solvent, together with the very mild operating conditions, make the protocol of interest for future industrial applications.

The data herein reported can be considered as a further advancement in the investigation of the NHPI-catalyzed radical oxidation of alkylaromatics, not only because they are in opposition to the Einhorn's results, but also because they confirm earlier mechanistic hypothesis like the importance of the equilibrium described in Eq. (13), and the electrophilic character of PINO compared to peroxy radicals.

## Acknowledgements

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