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Ethylbenzene Oxidation to its Hydroperoxide in the presence of N-Hydroxyimides and Minute Amounts of Sodium Hydroxide

***In memoriam* Dr. J.A. Delgado Oyagüe**

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ABSTRACT

N-hydroxyimides of the type N-hydroxyphthalimide (NHPI), N-hydroxysuccinimide (NHSI), N-hydroxymaleinimide (NHMI) and N-hydroxynaphthalimide (NHNI) were used in ethylbenzene oxidation with air under soft reaction conditions. The ethylbenzene conversion profile was found to increase almost linearly with time, and the rate of ethylbenzene conversion was the highest in the presence of NHNI. Nevertheless, the selectivity reached in all cases is still far from the values required for industrial application. On the other hand, the hydroperoxide yield increased dramatically with the addition of minute amounts of sodium hydroxide to the reaction mixture. It is worth noting that this increase can be associated to an enhancement in the selectivity to hydroperoxide because, in fact, ethylbenzene conversion slightly decreased with the addition of sodium. Indeed, this behavior is puzzling, because the amount of sodium is very small regarding ethylbenzene (0.005 mol %) and yet its effect is enormous. Finally, a tenfold increase in the concentration of N-hydroxyimide yielded only a slight increase in ethylbenzene conversion, but no improvement in hydroperoxide concentration. This behavior is related to the participation of >NO• radicals in the formation of by-products (alcohols and ketones) from hydroperoxide. Up to date, the combination of NHPI and NaOH produces the highest hydroperoxide yield reported.

KEYWORDS: Autoxidation, Organocatalysis, Homogeneous catalysis, Sodium hydroxide, Hydrocarbons, NHPI

INTRODUCTION

Autoxidation reactions are becoming increasingly important in industrial oxidation processes for several reasons: they are conducted with 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 avoids the generation of pollutants, as occurs with stoichiometric oxidants. Hydroperoxides are amongst the more interesting products of hydrocarbon autoxidation. These compounds are used as oxidizing agents of olefins and appear also as important precursors for the synthesis of phenols and other by-products. Ethylbenzene hydroperoxide is obtained by oxidizing ethylbenzene with air in liquid-phase, and it then employed in the epoxidation reaction of propylene at industrial scale [1-4]. The use of ethylbenzene hydroperoxide instead of cumene hydroperoxide or tert-butyl hydroperoxide has the advantage of co-producing styrene, even though its synthesis via autoxidation of ethylbenzene is much more difficult than the autoxidation of a hydrocarbon containing a tertiary C-atom. Thus, the process requires a suitable catalyst to minimize by-product formation.

Hydrocarbons autoxidations occur via free radical chain mechanism that hinders the control of selectivity. This free radical chain mechanism of hydrocarbon autoxidation has been widely documented [5-11]. The susceptibility of any substrate to autoxidation is determined by the $k_p/(2k_t)^{1/2}$ ratio, where k_p and k_t are, respectively, the specific rate constants of the propagation and termination reactions, which determine the length of the propagating chain and hence the reaction rate (see Scheme 1), because the addition of the alkyl radical (R•) to oxygen is extremely fast, in most cases being diffusion-controlled [6]. Alkylperoxy radicals, which are indeed the active propagating species, play a pivotal role within this scheme. In the course of the reaction, the hydroperoxide species formed act as radical initiators, which subsequently decompose, mainly into alcohoxy and hydroxy radicals. These two radicals react quickly with the hydrocarbon substrate to yield alkyl-type radicals. In the presence of molecular oxygen, these alkyl radical species react also quickly to form alkylperoxy radicals.

Notwithstanding hydroperoxide species are not only formed in the reaction but they are also consumed through the formation of new radicals (initiation step) and by the reaction with the (ROO•) chain propagating radicals [11]. This later reaction is claimed to be the major removal mechanism of the hydroperoxide, as well as the main route for ketone and alcohol production. The removal of the hydroperoxide by its dissociation into RO• and •OH radicals, as well as the formation of the ketone and aldehyde products by the ROO• + ROO• radical termination reaction have been both considered to be minor reaction pathways. In addition, as the classical mechanism cannot explain the experimental ketone/alcohol ratio of 2, a modified mechanism has been recently proposed [11] (Scheme 2).

An innovation in the aerobic oxidation of hydrocarbons through catalytic carbon radical generation under mild conditions has been achieved through the use of N-hydroxyphthalimide (NHPI) as a key compound, albeit requiring the presence of a transition metal compound [12-16]. In this oxidation, the phthalimide N-oxyl radical (PINO) generated *in situ* abstracts the H-atom from the hydrocarbon to form an alkyl radical, which is readily trapped by dioxygen and then forms oxygenated-compounds. The NHPI method is applicable in a broad variety of organic syntheses via carbon radical intermediates [12-16]. Nonetheless, some authors have described the use of NHPI in hydrocarbon autoxidation, in which it acts as a catalyst and does not require the presence of a transition metal compound [16, 17]. The fact that NHPI catalyzes hydrocarbon oxidation in the absence of a transition metal is of great importance in the synthesis of hydroperoxides, because the salts of cobalt, manganese and other transition elements decompose the hydroperoxides in the reactor giving rise to the formation of other O-containing compounds, such as ketones, acids, etc.

On the basis of experimental findings, this mechanism changes when NHPI acts as a catalyst (Scheme 3) [15, 17c, 20]. The PINO thus formed abstracts a hydrogen atom from the ethylbenzene to regenerate NHPI (reaction 5). The presence of NHPI in the reaction medium affords a new pathway for obtaining ethyl benzyl radicals (reaction 5), which reacts in the presence of molecular oxygen very rapidly to alkylperoxy radicals. The catalytic performance of NHPI splits this step in two ones as represented by reactions 5 and 6 in Scheme 3. Reaction 5 involves the formation of the ethyl benzyl radical, whereas reaction 6 accounts for the production of ethylbenzene hydroperoxide [21]. In general, the catalytic behavior of NHPI is related to the bond dissociation enthalpy (BDE) of its O-H bond that is either higher than or similar to the strength of the C-H bond cleaved [20, 22, 23].

In present industrial practice, ethylbenzene oxidation to its hydroperoxide is performed without solvent, using air as a source of oxygen, at temperatures ranging from 400 to 443 K, and slightly over atmospheric pressure to keep ethylbenzene in liquid phase (0.2 to 1.0 MPa) [24-29]. Another common practice is the addition to the reaction mixture of minute quantities of alkaline metals, such as sodium [24-27], alkaline-earth compounds, in particular barium [29, 30], or organic salts [31] to increase the yield to hydroperoxides.

However, to the best of our knowledge no systematic study of the sum of the catalytic effect of N-hydroxyimides and the minute quantities of sodium hydroxide in hydrocarbon autoxidation has been performed, especially in reaction conditions close to those of industrial practice.

Experimental

Reagents

Ethylbenzene (EB) with 0.4 wt% of ethylbenzene hydroperoxide (EBHP) was kindly provided by Repsol-YPF. Sodium hydroxide, N-hydroxyphthalimide (NHPI), N-Hydroxysuccinimide (NHSI), and N-Hydroxymaleimide (NHMI) were purchased from Sigma-Aldrich and N-Hydroxynaphthalimide (NHNI) from ABCR. All compounds were used without further purification.

Ethylbenzene Autoxidation

A one-liter steel reactor vessel (Zipperclave, Autoclave Engineers) was used to hold 520 g of 0.4 wt% of ethylbenzene hydroperoxide (EBHP) in ethylbenzene and the catalysts, if necessary. A nitrogen flow was passed through the reactor until no oxygen was detected at the reactor gas outlet by the online oxygen sensor (Servomex 5200), and then pressure and temperature were adjusted at 0.3 MPa and 421 K, conditions close to industrial practice [24-29], under stirring (1300 rpm). Once the temperature had reached a constant value, an air flow was bubbled through the mixture in the autoclave for 3 h. The air flow was controlled to keep an oxygen concentration at the autoclave gas outlet at 3 % by volume. This oxygen concentration is lower than the explosion and flammability limit of the reaction mixture. **CAUTION:** Since the autoxidation of hydrocarbons with molecular oxygen entails some risk, an important safety issue was considered in all the experiments.

The experimental conditions described in the preceding paragraphs indicate that the reaction was conducted outside the explosion limit of the reaction mixture. To keep the reaction in the safe region, it is very important to control oxygen concentration. In the event of an uncontrolled increase in oxygen concentration, an automatic safety system cuts in to cool the reactor temperature and feed nitrogen into the reactor.

The autoxidation of ethylbenzene (EB) at temperatures above 400 K is a typical autocatalytic chain reaction. At these temperatures, the decomposition of the EBHP to produce free radicals (Scheme 2) is one of the key steps in the oxidation reaction because it leads to an increase in the chain initiation rate and hence in the overall reaction rate. This is why small amounts of hydroperoxides are added in liquid-phase hydrocarbon oxidations: they act as radical initiators and remove the induction period just at the beginning of the reaction with molecular oxygen [11]. In view of this, all the kinetic experiments were performed by adding a small amount of EBHP (0.4 wt. %) to the reaction mixture. Even with this low concentration of EBHP, the amount of radicals in the reaction medium is enough to maintain the reaction rate at an almost constant level from the very beginning with no detectable induction period [11].

The wall effect on hydroperoxides formation is an important issue at laboratory scale, but it is precluded at industrial scale when working with large reactors for which the wall/volume ratio is too low. For this reason, the reactor was subjected to a passivation treatment. This treatment consisted to performing at least three consecutive ethylbenzene autoxidation reactions as to reach constant performance. In addition, a control reaction was regularly performed with the aim to detect any change in the reaction results.

The concentration of EBHP was measured by standard iodometric titration. The remaining organic compounds were analyzed by GC-FID on an Agilent Technologies 6890-plus device equipped with an HP-WAX capillary column. These samples were pretreated with triphenylphosphine (1:1 molar) to decompose the EBHP quantitatively to 1-phenylethanol (MBA) before GC analysis.

Ethylbenzene conversion (%) was defined as:

$$\mathrm{Conv}_{EB} = ([\mathrm{EBHP}] + [\mathrm{MBA}] + [\mathrm{ACP}])/[\mathrm{EB}]_0 \times 100 \qquad 1$$

where [EBHP], [MBA] and [ACP] are the molar concentrations of EBHP, MBA and acetophenone (ACP), respectively, in the sample and $[EB]_0$ is the initial molar concentration of ethylbenzene. EBHP selectivity (%) can be defined as:

$$S_{EBHP} = [EBHP]/([EBHP] + [MBA] + [ACP]) \times 100 \qquad 2$$

where the acronyms between square brackets have the same meaning as in the previous paragraph.

RESULTS AND DISCUSSION

In this study, we have selected four N-hydroxyimides (Scheme 4). These compounds present dissimilar bond dissociation energy (BDE) of NO-H (Table 1). Several values of BDE are reported in literature, but there is reasonable agreement in the order of the BDE, whatever the source or calculation method employed, solvent presence or gas phase calculation performed. The BDE order generally accepted is NHNI > NHSI > >NHPI~NHMI. However, this order cannot be simply extrapolated to a reactivity order because other factors must be taken into account; a higher NO-H BDE will obviously make reaction 5 of Scheme 3 faster, but will simultaneously result in a lower equilibrium concentration of the >NO• radicals (reaction 6, Scheme 3).

We began by studying the catalytic effect of these compounds with a very small amount of N-hydroxyimides (0.6 mM, 0.0072 mol % regarding ethylbenzene), which is two orders of magnitude lower than that employed in previous works [17]. We decided to proceed in this way because N-hydroxyimides, as homogenous catalysts, will remain in solution in the final product and the presence of certain amounts of catalyst can affect later use of ethylbenzene hydroperoxide. Ethylbenzene hydroperoxide is not an end product and will be used as an oxygen carrier to oxidize other substrates, usually propene to 1,2-epoxypropane [1-3].

These N-hydroxyimides were employed in ethylbenzene oxidation with air under moderate pressure and temperature. Furthermore, a blank experiment was conducted without the addition of N-hydroxyimides in order to obtain reaction results in the absence of catalyst. The ethylbenzene conversion profile (Figure 1) increased almost linearly with time; in all cases, ethylbenzene conversion was higher when N-hydroxyimide is present. The slopes of conversion versus time profiles are different among the N-hydroxyimides used. In a first approach, reaction rate runs in parallel with the BDE of the NO-H bond of the N-hydroxyimide. In other words, a fairly strong O-H bond is necessary condition to abstract an H-atom from ethylbenzene (reaction 5 of Scheme 3) and therefore to have a highly active N-hydroxyimide catalyst. However, a too strong O-H bond would decrease the equilibrium concentration of the NO• radicals (reaction 6 of Scheme 3). Accordingly, the optimized O-H bond energy may explain the activity order observed in the target reaction: blank < NHPI < NHMI < NHSI < NHMI.

It can be seen that the change in the concentration of EBHP does not follow the same trend as ethylbenzene conversion (Figure 1). At short reaction time, the hydroperoxide concentration increases linearly, but at high reaction times the slope clearly diminishes. Due to these crossed effects, the selectivity to hydroperoxide obtained depends on the catalyst employed (Figure 2). There is not a clear relation between the BDE of the NO-H in the N-hydroxyimide used and the selectivity to hydroperoxide. NHNI presents a different behavior; the EBHP selectivity reached is clearly higher than that obtained for the other N-hydroxyimides. This effect can be associated to the very high BDE of the NO-H bond for NHMI. In consequence, the equilibrium of reaction 6 of Scheme 3 is shifted to the formation of >NOH + EBHP, and hence the concentration of >NO• radicals in the reaction media decreases, and is well known that this radical participates in the formation of by-products (alcohols and ketones) from hydroperoxide [20c, 23, 33]. For this reason, the amount of byproducts formed from hydroperoxide is lower and the selectivity to EBHP is higher. However, the selectivity reached in all cases is still far from the desired values for an industrial application; this lower selectivity in absence of sodium hydroxide has been widely documented [24-28].

For this reason, we decided add minute quantities of sodium to the reaction mixture, as it is well documented that sodium salts increase the yield to hydroperoxides [24-29]. The addition of a minute quantity of sodium, as NaOH, leads to a dramatic increase in the hydroperoxide yield (Table 2, Figure 2), this effect was reported previously in the literature [24-29]. Another interesting effect is the change in the hydroperoxide concentration profile, the EBHP concentration increases linearly with reaction time, which contrasts with the changes brought about in absence of sodium hydroxide. Nevertheless, it is worth noting that this increase is due to changes in the selectivity to hydroperoxide because ethylbenzene conversion is in fact decreased by the addition of sodium. This effect is puzzling, because the amount of sodium is very small regarding ethylbenzene (0.005 mol %), yet it has an enormous impact. The modification in the selectivity of EBHP in the presence of sodium is due to a decrease in the consumption of ethylbenzene accompanied with an increase in the EBHP yield (Table 3, Figure 3 and Figure 4). This effect is even more pronounced in blank, NHPI and NHSI experiments. Sodium hydroxide quickly reacts with organic acids present in the reaction mixture and hence the effect of sodium hydroxide addition is due to the presence of sodium salts of organic acids, mainly benzoic acid. Similar results have been obtained using other sodium salts, i.e. carbonate or benzoate.

For this reason, a deep analysis of the reaction results has been performed in order to study the effect of sodium hydroxide in the reaction. The [MBA]/[EBHP] vs. ACP]/[EBHP] plots (Figure 5) derived from the experiments in absence and presence of NaOH both exhibit a near-perfect linear relationship, consistent with the mechanism proposed [11]. According to equation taking from literature [11]:

$$\frac{[MBA]}{[EBHP]} \approx \frac{b}{a}(1+e) + \frac{d}{a}(1+e)\frac{[ACP]}{[EBHP]}$$

“a”, “b”, “c” and “d” are the rate of different reactions in the proposed mechanism (Scheme 2) and “e” is the rate of H-abstraction of ethylbenzene by an alcohoxyl radical, an estimated value of “e” ≈ 0.9 for this radicals and hydrocarbons have been reported [11]. The slopes in absence and presence of NaOH are similar, i.e. 0.46 and 0.38, respectively, and close to the value of 0.43 reported in literature [11]. On the other hand, the Y-axis intercepts differ greatly, i.e. 0.08 in absence versus only 0.008 in presence of NaOH; the later value is close to the result of 0.006 +/- 0.002 reported previously [11], even though the former being much higher. Thus, it appears that the presence of sodium hydroxide affects greatly the ratio b/a (see Scheme 2) but to a much lesser extent the ratio d/a. This observation indicates that reaction 3 of Scheme 2 is clearly affected by the presence of sodium hydroxide, and if present route “a” is favored respect route “b” (Scheme 2). This results in the formation of a higher concentration of hydroperoxide respect to alcohol and ketone by-products.

Finally, we studied the effect of increasing N-hydroxyimide concentration for the two most promising candidates NHPI and NHSI, with this concentration being closer to the one used in previous works [17]. A significant increase in the concentration of N-hydroxyimide (10 times) yields a slight increase in ethylbenzene conversion and EBHP concentration (Figure 6 and Table 4), but this rise is very small in comparison with the increase in N-hydroxyimide concentration. A decrease in hydroperoxide selectivity is clearly observed for the higher concentration studied (Figure 7 and Table 4). These behavior can be related with the participation of >NO• radicals in the formation of by-products (alcohols and ketones) from hydroperoxide, [20c, 23, 33]. Consequently, an increase in N-hydroxyimide concentration produces a rise in ethylbenzene conversion due to the growth in catalyst concentration, but this increase is small as compared with the higher amount of N-hydroxyimide fed, because part of this catalyst is not employed in the main reaction but it is consumed in by-products formation.

CONCLUSIONS

From both the approach and results obtained in the present work, the following conclusions can be drawn:

(i) Ethylbenzene oxidation to its hydroperoxide has been efficiently performed from both economic and environmental viewpoints using a green oxidant (air) under moderate pressure and temperature (421 K and 0.3 MPa), in presence of N-hydroxyimides as radical initiators and in the absence of any solvent.

(ii) For all the hydroxyimides (NHPI, NHSI, NHMI and NHNI) explored, the ethylbenzene conversion profile was found to increase almost linearly with time; the activity order observed in reaction was: NHPI < NHMI < NHSI < NHMI. This order of reactivity does not follow the trend of BDE of NO-H bond. A strong O-H bond facilitates the abstraction of an H-atom from ethylbenzene (reaction 5 of Scheme 3), but simultaneously decreases the equilibrium concentration of the NO• radicals (reaction 6 of Scheme 3).

(iii) Incorporation of minute quantities of sodium hydroxide (0.005 mol %) led to a dramatic increase in hydroperoxide yield. Indeed, this increase in yield is associated to changes in the selectivity to hydroperoxide because, in fact, ethylbenzene conversion is depleted by the addition of sodium. In spite of the puzzling beneficial effect of minute amounts of sodium, we believe that the presence of sodium hydroxide affects greatly the ratio of fractions b/a (see Scheme 2), but to a much lesser extent the ratio d/a, as depicted by equation 3 [11]. This observation indicates that the reaction 3 of Scheme 2 is clearly affected by the presence of sodium hydroxide and, if present, route "a" is favored respect route "b" (Scheme 2), thus increasing the yield of hydroperoxide respect other alcohol and ketone by-products.

(iv) The combination of NHPI and small amounts of NaOH leads to an increase in the yield to ethylbenzene hydroperoxide clearly higher than the present state of the art.

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Table 1 Bond dissociation energy (BDE) of NO-H taken from the literature of the N-hydroximides used in this study.

N-hydroximide	BDE (Kcal/mol)	Reference
NHPI	81.2	23 (Theoretical DFT)
NHMI	81.2	23 (Theoretical DFT)
NHSI	86.0	23 (Theoretical DFT)
NHNI	87.6	23 (Theoretical DFT)
NHPI	83.5	22 (Theoretical G3B3)
NHMI	83.5	22 (Theoretical G3B3)
NHPI	88.1	20a (Experimental)

Table 2 Results in the oxidation of ethylbenzene (180 min) with air at 421 K, 0.3 MPa using different N-hydroximides (0.6 mM), with or without NaOH.

	Sodium Hydroxide	% Ethylbenzene Conversion	Concentration of EBHP (wt%)	% Selectivity to EBHP	EBHP Yield[a] (mol/h)
Blank	---	20.9	7.4	25.8	0.135
	1 ppm	14.2	11.6	72.6	0.170
NHPI	---	24.9	6.2	24.6	0.101
	1 ppm	21.3	14.9	77.3	0.201
NHMI	---	27.2	7.8	26.4	0.163
	1 ppm	23.8	10.8	45.9	0.179
NHSI	---	30.2	5.9	19.2	0.133
	1 ppm	16.0	13.5	82.3	0.176
NHNI	---	31.8	11.0	40.8	0.219
	1 ppm	17.9	12.7	60.6	0.156

[a] Hydroperxide yield was calculated at short reaction time.

Table 3 Ethylbenzene consumption and EBHP TOF in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroximides (0.6 mM), with or without sodium hydroxide.

	TOF[a] EB Consumption (h^{-1})		TOF[a] EBHP production (h^{-1})	
	---	Na^+ (1 ppm)	---	Na (1 ppm)
Blank	981	678	375	472
NHPI	1169	850	281	558
NHMI	1300	1119	453	497
NHSI	1381	728	369	489
NHMI	1414	825	608	433

[a] TOF was calculated over short reaction time.

Table 4 Results in the oxidation of ethylbenzene (180 min) with air at 421 K, 0.3 MPa using different N-hydroximide concentration and 1 ppm of Na^+.

	N-hydroximide concentration	% Ethylbenzene Conversion	Hydroperoxide Concentration (wt%)	% Selectivity to hydroperoxide
Blank	---	14.2	11.6	72.6
NHPI	0.6 mM	21.3	14.9	77.3
	6 mM	23.2	18.3	68.9
NHSI	0.6 mM	16.0	13.5	82.3
	6 mM	19.4	15.6	77.3

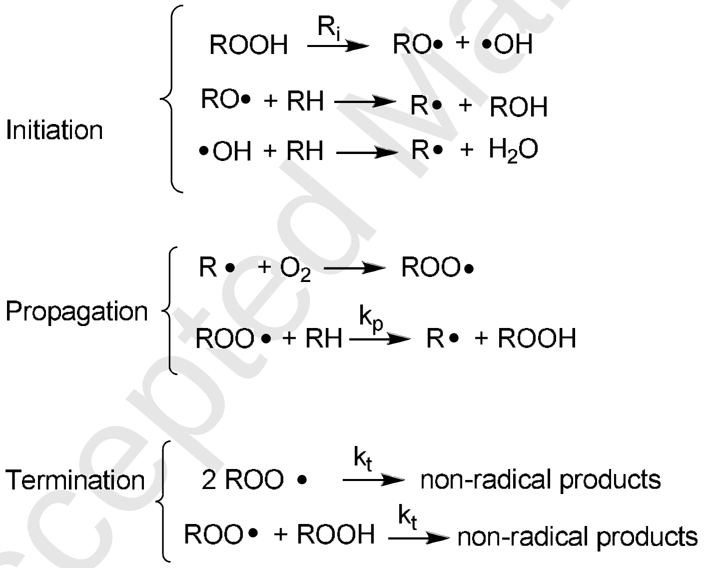
SCHEME TITLES

Scheme 1 Standard autoxidation mechanism in presence of hydroperoxide

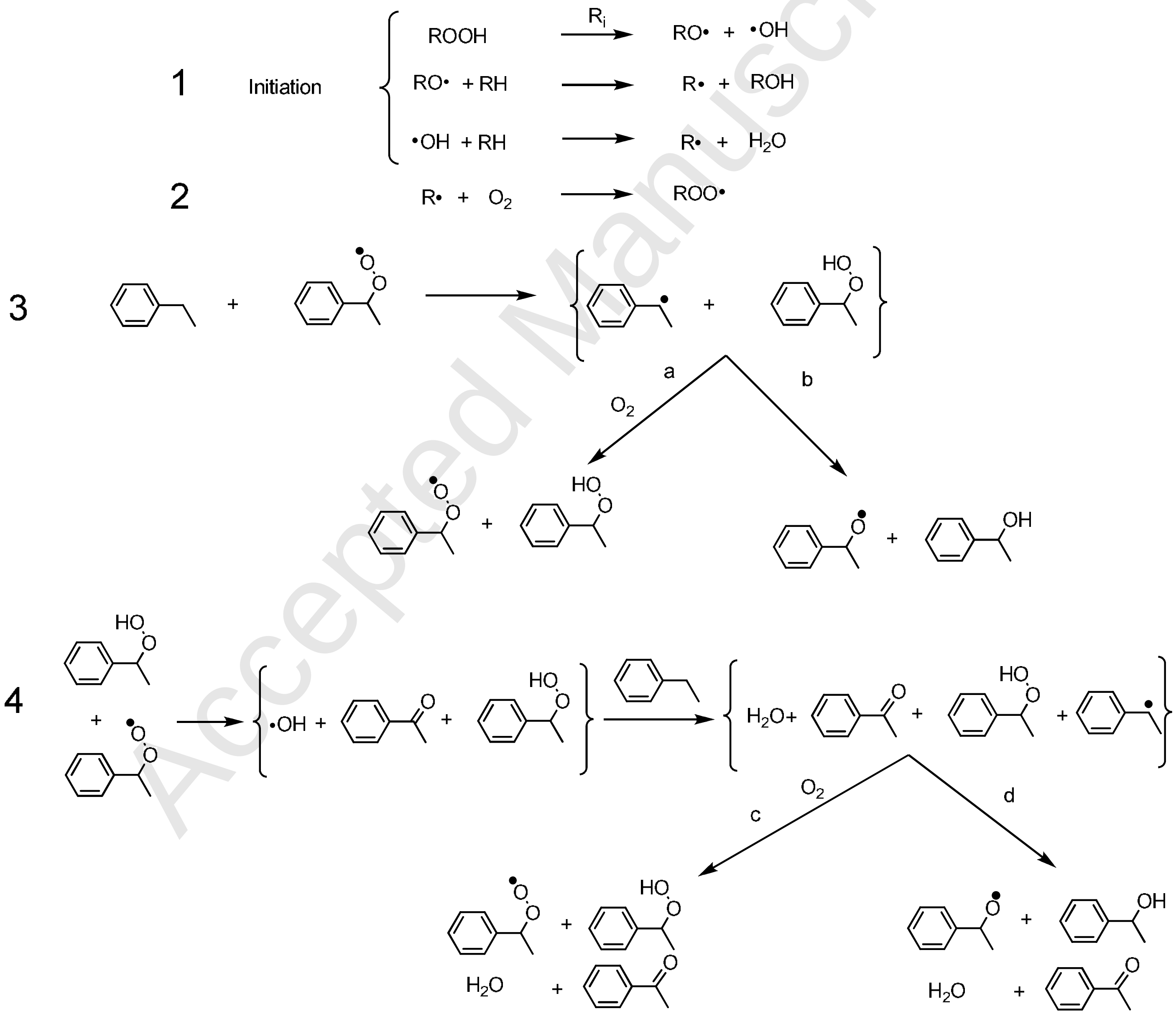
Scheme 2 Free radical mechanism of ethylbenzene autoxidation based on reference 11

Scheme 3 Additional steps of the radical mechanism of ethylbenzene autoxidation due to the presence of NHPI

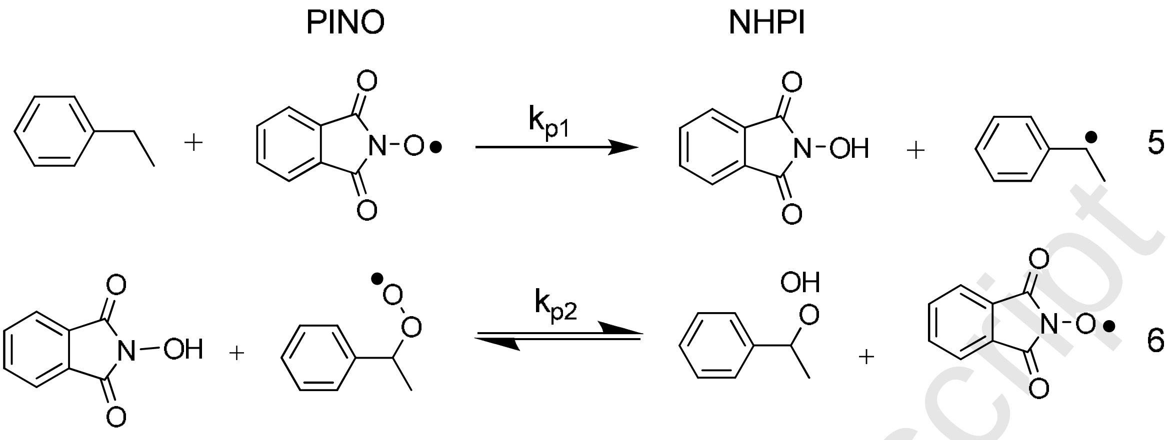
Scheme 4 N-hydroxyimides used in the study



Scheme 1


1
Initiation
ROOH
Ri
RO• + •OH
RO• + RH
R• + ROH
•OH + RH
R• + H2O
2
R• + O2
ROO•
3
+
O
O
HO
a
b
O2
OH
4
•OH +
H2O+
c
d
H2O
+

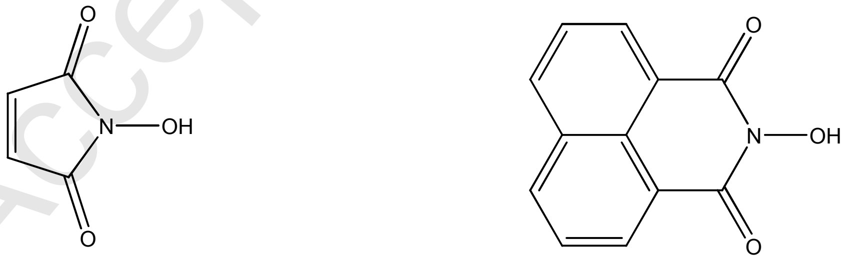
Scheme 2



Scheme 3


N-Hydroxyphthalimide (NHPI)

N-Hydroxysuccinimide (NHSI)


N-Hydroxymaleimide (NHMI)

N-Hydroxynaphthalimide (NHNI)

Scheme 4

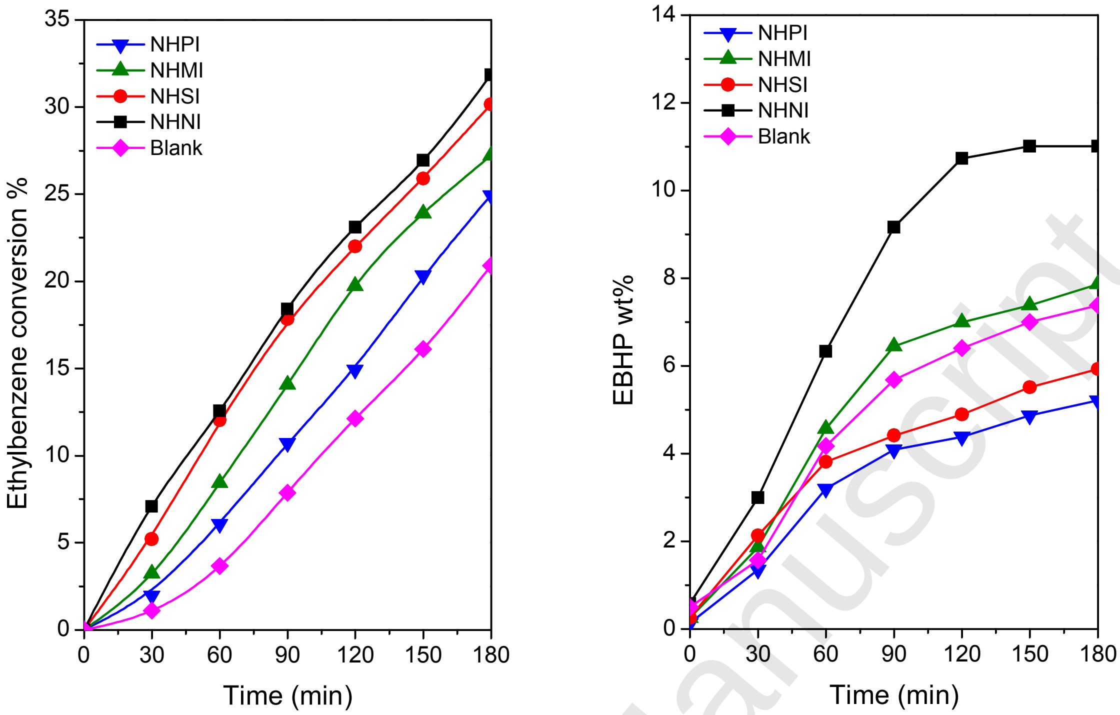


Figure 1 Evolution of ethylbenzene conversion and hydroperoxide concentration versus time in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimides (0.6 mM).

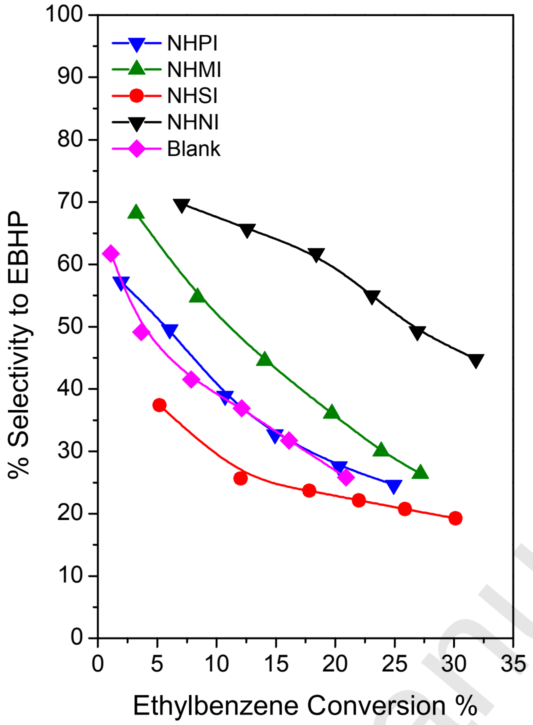


Figure 2 Evolution of the selectivity to hydroperoxide versus ethylbenzene conversion in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimides (0.6 mM).

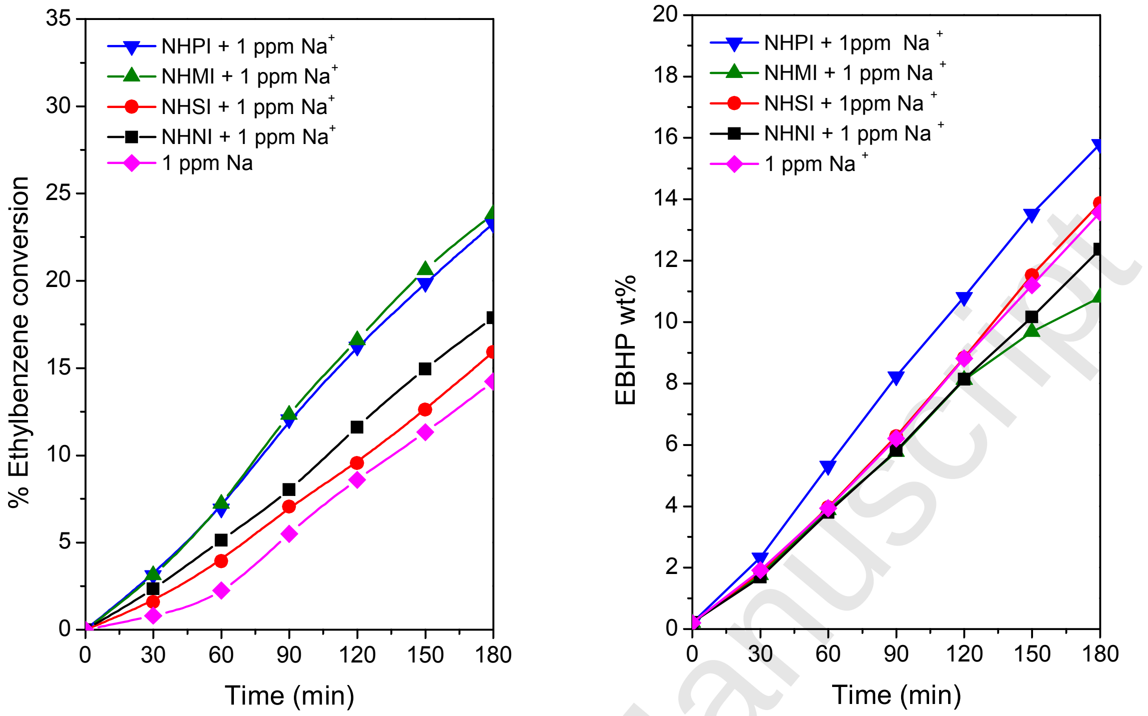


Figure 3 Evolution of ethylbenzene conversion and hydroperoxide concentration versus time in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimides (0.6 mM) and 1 ppm of Na^+.

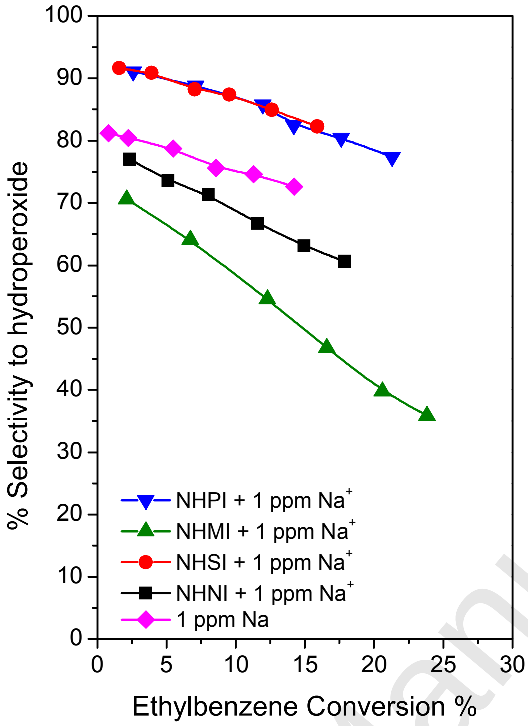


Figure 4 Evolution of the selectivity to hydroperoxide versus ethylbenzene conversion in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimides (0.6 mM) and 1 ppm of Na^+.

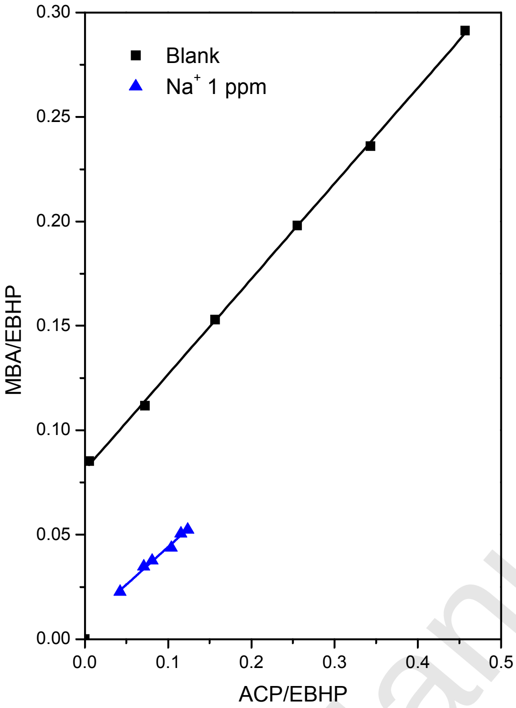


Figure 5 [MBA]/[EBHP] versus [ACP]/[EBHP] in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa in presence or not of 1 ppm of Na^+.

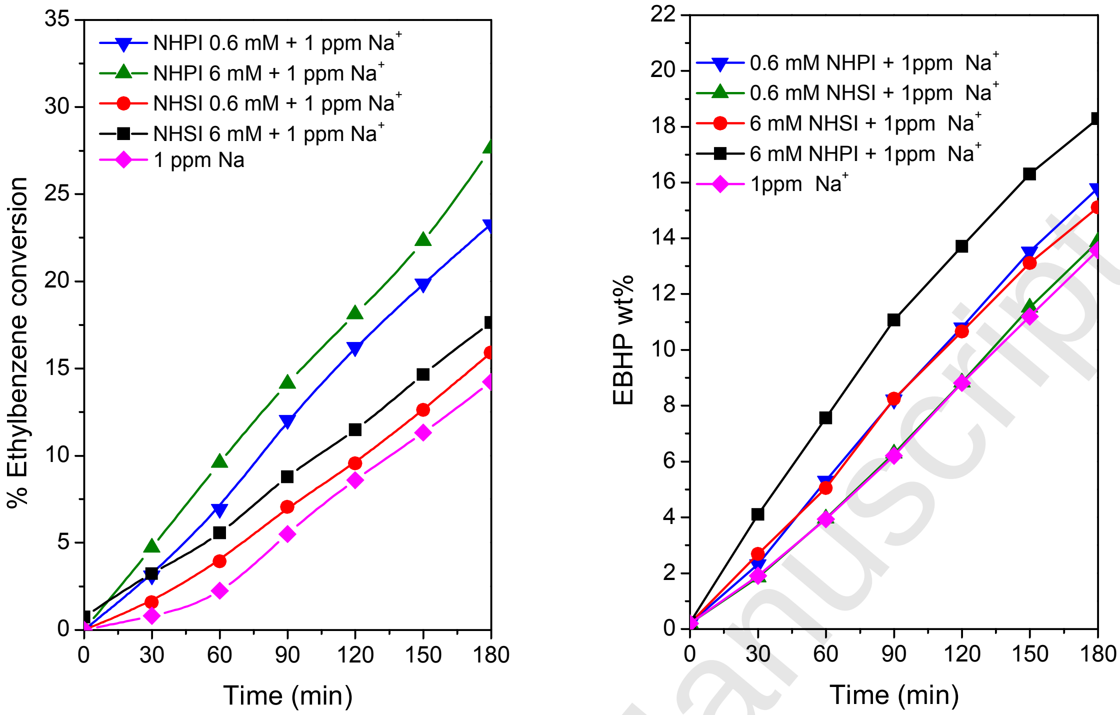


Figure 6 Evolution of ethylbenzene conversion and hydroperoxide concentration versus time in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimide concentration and 1 ppm of Na$^+$.

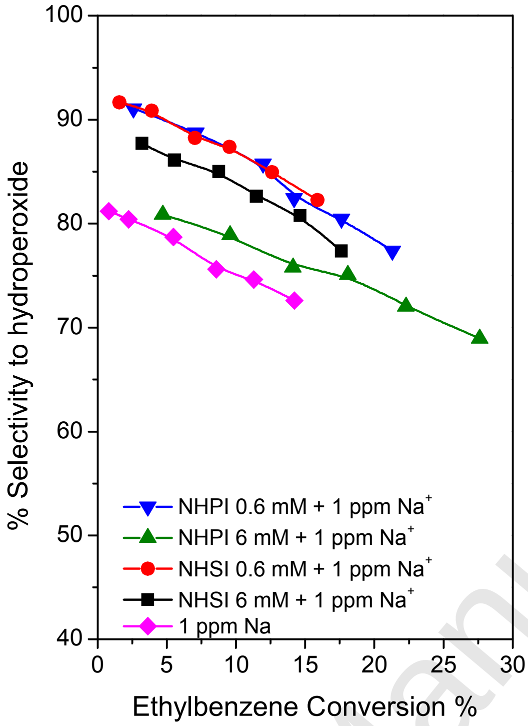
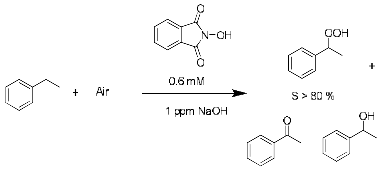


Figure 7 Evolution of the selectivity to hydroperoxide versus ethylbenzene conversion in the oxidation of ethylbenzene with air at 421 K, 0.3 MPa using different N-hydroxyimide concentration and 1 ppm of Na^+.

Graphical Abstract:



Ethylbenzene Oxidation to its Hydroperoxide in the presence of N-Hydroxyimides and Minute Amounts of Sodium Hydroxide.

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N-hydroxyimides were used in ethylbenzene oxidation with air under soft reaction conditions. The ethylbenzene conversion increase in the presence of the organocatalysts. On the other hand, the hydroperoxide yield increased dramatically with the addition of a minute quantity of sodium hydroxide to the reaction mixture. Combination of NHPI and NaOH produce the highest yield to hydroperoxide reported.