

Liquid-phase ethylbenzene oxidation to hydroperoxide with barium catalysts

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Received 29 July 2004; received in revised form 4 October 2004; accepted 5 October 2004

Available online 23 November 2004

Abstract

Barium compounds (barium oxide, barium acetylacetonate, barium nitrate) have been used as catalysts for the liquid-phase oxidation of ethylbenzene with molecular oxygen. Ethylbenzene hydroperoxide (EBHP) was the major product, although small amounts of acetophenone (ACP) and 1-phenylethanol were also formed, indicating that C–H bond activation takes place only at the alkyl chain. For barium oxide, the rate of EBHP formation was found to increase with the barium concentration up to 1 ppm Ba, thereafter decreasing at higher concentrations. The type of barium compound influenced the rate of EBHP formation to a significant extent. As a general rule, non-basic barium salts, such as nitrate and acetylacetonate, led to a decrease in the EBHP yield and also to a decrease in ethylbenzene conversion; although in the latter case it was less marked. This finding can be interpreted as being due to the partial decomposition of EBHP, under the experimental conditions employed in the present work, into ACP and 1-phenylethanol.

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Keywords: Ethylbenzene; Autoxidation catalysis; Ethylbenzene hydroperoxide; Barium compounds

1. Introduction

Replacing stoichiometric oxidants such as KMnO_4 , Ag_2O and CrO_3 by less environmentally damaging compounds is self-evidently a sensible chemical strategy. Doing this catalytically, with alkyl-hydroperoxides or hydrogen peroxide as the oxidants, is an even better method, but best of all would be to develop catalysts that selectively oxidise hydrocarbons using either molecular oxygen or air under mild conditions.

Hydroperoxides are used not only as oxidizing agents of olefins but also as important precursors for the synthesis of phenols. For instance, α -hydroperoxy-ethylbenzene, obtained by aerobic oxidation of ethylbenzene, is used as an active oxygen carrier in the epoxidation of propylene,

which is known as the PO/SM (propylene oxide/styrene co-production) process [1]. The cumene-phenol process (Hock process), based on the decomposition of cumene hydroperoxide with sulphuric acid to phenol and acetone, is currently used worldwide for phenol synthesis [2].

The free radical chain mechanism of hydrocarbon autoxidation is well documented [3–5]. The kinetics of hydrocarbon (RH) oxidation by O_2 is to a large extent determined by the rate of chain initiation and its change during oxidation [3–7] (Scheme 1). As a general rule, chain initiation in autoxidation processes is associated with reactions of hydroperoxides (ROOH), which are the primary products of RH oxidation.

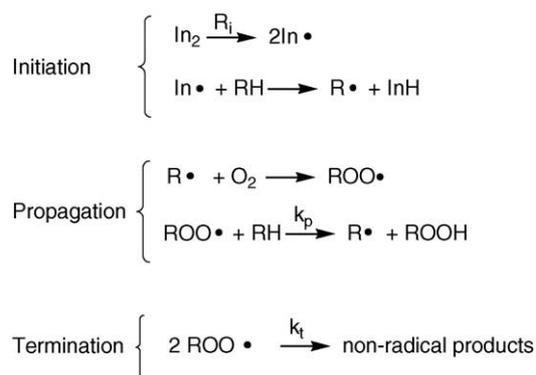
A broad variety of homogeneous catalytic systems has been described in the literature for this reaction [8–13]. In the patents literature, some authors have proposed the use of minute quantities of alkaline metals, such as sodium, to increase the yield to organic hydroperoxides in the autoxidation of hydrocarbons [14], while others have posited the use of alkaline-earth compounds [15], in particular barium, an increase in hydroperoxide selectivity being observed when

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Scheme 1. Standard autoxidation mechanism.

an alkaline-earth salt is added to the reaction mixture. However, to the best of our knowledge no systematic study of the catalytic effect of these compounds in hydrocarbon autoxidation can be found in the open technical literature. Copper tri- and tetraaza macrocyclic complexes encapsulated in zeolite-Y also exhibit good catalytic performance in the oxidation of ethylbenzene [16] using *tert*-butyl hydroperoxide as oxidant. In this case, acetophenone was the major product, although small amounts of *o*- and *p*-hydroxyacetophenones were also formed, indicating that C–H bond activation takes place both at benzylic and aromatic ring carbon atoms. In addition, the kinetics and mechanism of ethylbenzene (and other olefin and lipid) liquid-phase oxidations by molecular oxygen have been studied. For the latter reactions, ionic surfactants were found to affect the rate and mechanism of hydroperoxide decay, and consequently the rate of the ethylbenzene oxidation [17].

In keeping with the above, this work was undertaken to study in greater depth the effect of the addition of barium compounds on the behaviour of the yield of ethylbenzene hydroperoxides during the oxidation of ethylbenzene with molecular oxygen. Through analysis of the effects of the barium and oxygen concentrations and also of the nature of the barium compounds, greater insight into the mechanism of ethylbenzene liquid-phase oxidation has been gained.

2. Experimental

All reactions were carried out in a 150 ml thermostatable glass cylindrical vessel provided with a glass stirrer and a gas inlet system, a type-K thermocouple, and a water-cooled reflux condenser. Temperature was controlled by a heating circulation bath (Julabo MV-4); the stirrer was powered by a variable speed motor (Heidolph HP-1), and gases were fed to the reactor through mass flow controllers (Bronkhorst HI-TEC). In a typical oxidation run, 50 g of EB containing about 0.4 wt.% of EBHP (kindly provided by Repsol-YPF) and the amount of barium compound designed for the experiment were loaded into the reactor, after which the heating bath and stirring speed were set at the desired values (typically

403 K and 1000 rpm). BaO, Ba(acac)₂ and Ba(NO₃)₂ compounds (Merck, reagent grade) were used as catalyst precursors. Since the barium compound was incorporated at levels of ppm, it was added to the reaction mixture from a saturated aqueous solution. Once temperature had reached a constant value, gas flow was set and kept constant during the experiment. Aliquots were taken at 0, 60, 120, 180, 240 and 300 min of reaction. The total amount withdrawn from the reactor was less than 10% of the total reaction mixture. The concentration of EBHP was measured by standard iodometric titration. The remaining organic compounds were analysed by GC-FID on a Agilent Technologies 6890-plus gas chromatograph (GC) equipped with an HP-WAX capillary column. Before GC analysis, these samples were pretreated with triphenylphosphine (1:1 molar) to quantitatively decompose the EBHP to 1-phenylethanol. Ethylbenzene conversion (C_{EB}) and EBHP selectivity (S_{EBHP}) were defined as follows:

$$C_{\text{EB}} = \frac{[\text{EBHP}] + [\text{MBA}] + [\text{ACP}]}{[\text{EB}]_0} \times 100 \quad (1)$$

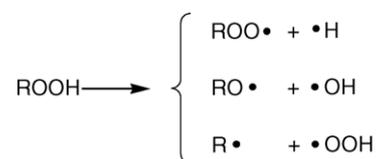
$$S_{\text{EBHP}} = \frac{[\text{EBHP}]}{[\text{EBHP}] + [\text{MBA}] + [\text{ACP}]} \times 100 \quad (2)$$

where [EBHP], [MBA] and [ACP] are the molar concentrations of ethylbenzene hydroperoxide, 1-phenylethanol and acetophenone, respectively, in the sample and [EB]₀ is the initial molar concentration of ethylbenzene.

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 is conducted above the explosion limit of the reaction mixture. To avoid this hazard, two precautions were taken: (i) a flow of nitrogen was fed just over the surface of the liquid, and (ii) the effluent oxygen concentration was continuously monitored with an oxygen sensor and kept almost constant at approximately 1 vol%. In any case, the laboratory glassware was used behind safety screens, and the reaction volume was limited to 50 g solutions.

3. Results and discussion

The autoxidation of ethylbenzene (EB) at 403 K is a typical autocatalytic chain reaction. At this temperature, 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



Scheme 2. Different radical products of the decomposition of hydroperoxide.

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. In view of this, all the kinetic experiments were performed upon 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.

First, the effect of the barium oxide concentration was studied. Representative kinetic plots of EBHP accumulation during ethylbenzene autoxidation in the presence of variable amounts of barium oxide ranging from 0.5 to 32 ppm are shown in Fig. 1. From this figure it is apparent that the EBHP yield increases from 0.5 to 1 ppm Ba, then decreasing at higher barium oxide concentrations. Although very little is known about the influence of barium oxide in EB autoxidation, this result is in keeping with claims in the patents literature indicating a detrimental effect of concentrations of alkaline and alkaline-earth elements above approximately 30 ppm [14] on EBHP accumulation in liquid-phase during the autoxidation reaction of ethylbenzene.

In the next step, we analysed the influence of the type of barium compound in the behaviour of ethylbenzene autoxidation. For this purpose, not only barium oxide but also barium nitrate and barium acetylacetonate salts were used. These salts have different acid–base properties, and hence different types of kinetic behaviour in ethylbenzene oxidation are expected to occur, depending on the type of the barium salt added to the reaction mixture.

The performance of these three barium compounds in the liquid-phase oxidation of ethylbenzene is shown in Fig. 2.

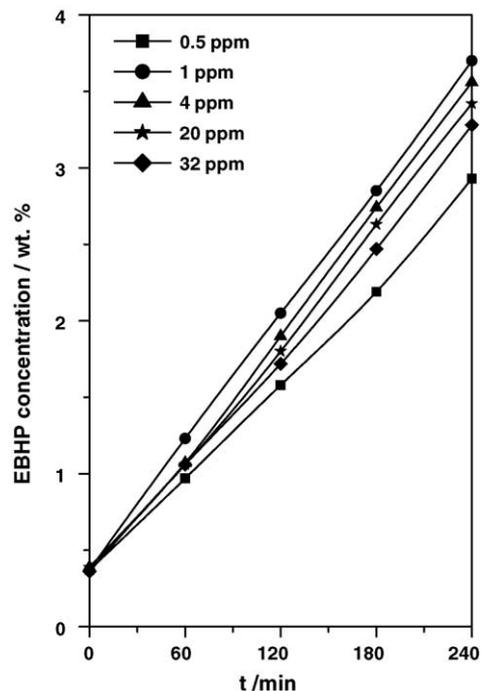


Fig. 1. Effect of the barium oxide concentration on the ethylbenzene hydroperoxide concentration profile during ethylbenzene autoxidation at 406 K with air.

When the reaction was conducted in the presence of the non-basic compounds ($\text{Ba}(\text{NO}_3)_2$ and $\text{Ba}(\text{acac})_2$) a decrease in the EBHP yield was observed (Fig. 2a). This decrease was more pronounced for $\text{Ba}(\text{NO}_3)_2$ than for the $\text{Ba}(\text{acac})_2$ salts. This finding is consistent with patent literature claims, which recommend the use of alkaline basic compounds (hydroxides or carbonates) for increasing the EBHP with respect to neutral compounds [18,19]. The results shown in Fig. 2 clearly

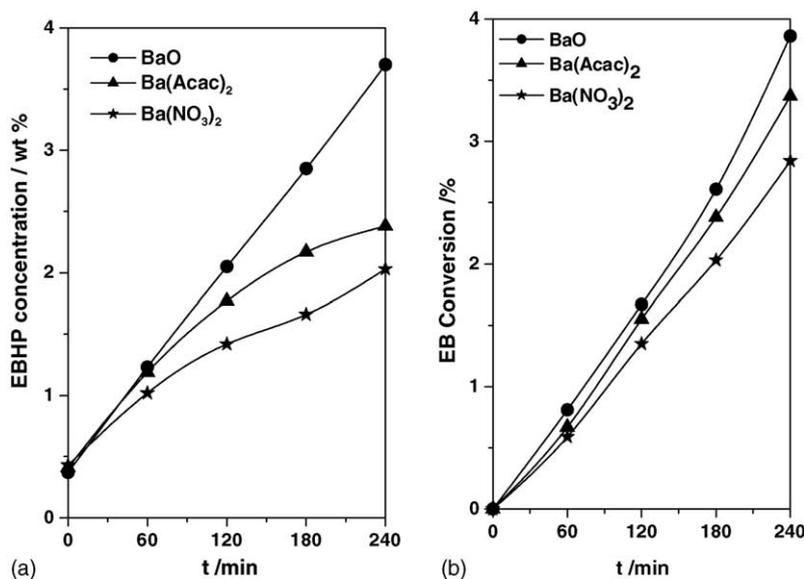


Fig. 2. Effect of the barium compound on the behaviour of ethylbenzene autoxidation at 406 K with air: (a) ethylbenzene hydroperoxide concentration, (b) ethylbenzene conversion.

indicate that the decrease in the EBHP yield becomes more marked at higher concentrations of EBHP, suggesting that small amounts of compounds of basic character would be able to stabilize EBHP against its decomposition. The decrease in the EBHP yield was less marked than that of ethylbenzene (EB) conversion (Fig. 2b). This was more evident when Ba(acac)₂ was added to the reaction mixture. In this case, EBHP was substantially lower than when using BaO, although ethylbenzene conversion was similar in both cases. This finding implies that part of the EBHP was decomposed to secondary products, such as 1-phenylethanol or acetophenone. Barium nitrate led not only to a lower ethylbenzene conversion to 1-phenylethanol and acetophenone but also to a lower EBHP yield. Both facts may be related to each other, since the lower concentration of EBHP, which acts as a radical initiator in the autoxidation reaction, brings about a de-

crease in the formation of radicals and hence in the reaction rate.

The effect of the partial pressure of oxygen on ethylbenzene conversion and hydroperoxide selectivity in the presence of 1 ppm of BaO was also studied. The molar concentration of oxygen in the feed gas was varied between 21 (air) and 70%; the results are shown in Fig. 3. The increase in the oxygen concentration led to an enhanced EBHP yield (Fig. 3a). However, at high concentrations of EBHP it tended to decay, in particular for oxidation with 70% of O₂. In fact, the fall in the EBHP yield at higher concentrations has been described previously [5]. According to the patents literature, this drawback was apparently resolved by using different reactor vessels with decreasing profiles of the reaction temperature among the vessels [20]. An increase in the oxygen concentration in the feed gas fed also led to an increase in the

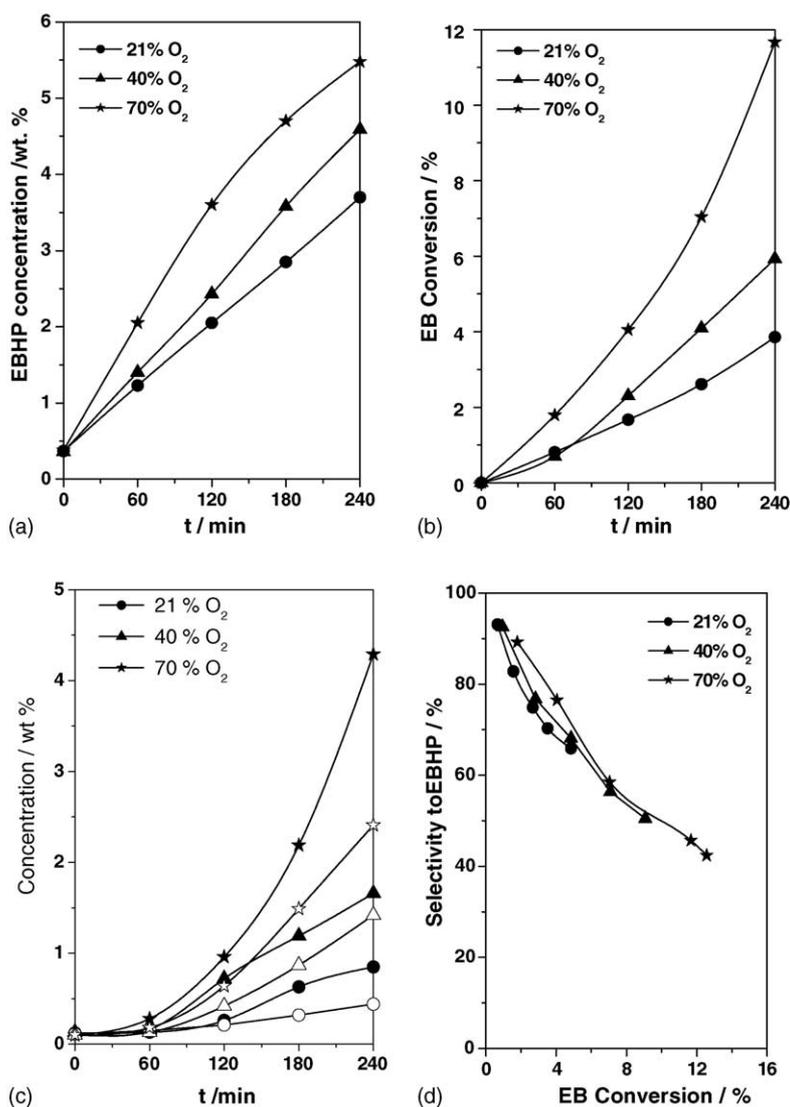


Fig. 3. Effect of the oxygen concentration on the behaviour of ethylbenzene autoxidation at 406 K with the barium oxide catalyst (1 ppm). (a) Ethylbenzene hydroperoxide concentration, (b) ethylbenzene conversion, (c) concentration of acetophenone (filled) and 1-phenylethanol (unfilled), (d) selectivity to hydroperoxide.

ethylbenzene conversion (Fig. 3b), this being higher at higher O₂ concentrations. In parallel with ethylbenzene conversion, formation of other products, such as acetophenone or 1-phenylethanol, was also observed (Fig. 3c). Acetophenone was the main secondary product with a concentration higher than that of 1-phenylethanol. Acetophenone could be formed directly in the termination reaction step [2–6] or by the oxidation of 1-phenylethanol. Apparently, the selectivity to EBHP was the lowest for the highest oxygen concentration at the end of the experiment (4 h). When air was fed, the selectivity to EBHP was 66%, but decreased to 51 and 43% in the presence of 40 and 70% oxygen, respectively, in the feed stream. However, careful scrutiny of the selectivity to EBHP versus conversion (Fig. 3d) revealed that selectivity, at the same conversion level, was similar for the three oxygen concentrations studied, and the differences observed were due to different conversion levels. This type of behaviour is consistent with the autoxidation mechanism of hydrocarbons in liquid-phase [4–6]. According to this scheme, the 1-phenylethanol and acetophenone by-products come directly from the radical species present in the reaction medium (termination step), without the participation of oxygen in this step.

4. Conclusions

The data obtained in this work indicate that the kinetics of ethylbenzene liquid-phase oxidation is feasible in the presence of barium compounds at ppm levels. Several parameters, including the concentration of the barium compound, its nature, and the concentration of oxygen, affect both the reaction rate of ethylbenzene conversion and hydroperoxide decay. More specifically, (i) ethylbenzene oxidation to the corresponding peroxide was found to be highly selective in the presence of BaO within the 0.5–32 ppm concentration range, with a maximum at 1 ppm; (ii) among the three barium compounds investigated, barium oxide was the most efficient and their reactivity trend followed an order of: BaO > Ba(acac)₂ > Ba(NO₃)₂; (iii) finally, a rise in the oxygen concentration in the gas feed stream enhanced ethylbenzene conversion while maintaining selectivity to EBHP at a high level when it was compared at the same ethylbenzene conversion level.

Acknowledgments

The authors acknowledge financial support from Repsol-YPF (Spain). JMCM gratefully acknowledge financial support from the Ministerio de Ciencia y Tecnología (Spain) in the Ramon y Cajal Program. We wish to thank to Dr. Juan Antonio Delgado Oyagüe for his helpful discussions.

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