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Photoxidation of ethylbenzene with air catalyzed by a polymer supported Rose Bengal photosensitizer

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Abstract

This paper deals with the liquid-phase photoxidation of ethylbenzene with air to give ethylbenzene hydroperoxide, irradiating with a 500 W tungsten halogen lamp and using a polymer supported Rose Bengal photosensitizer, in a stirred tank reactor at atmospheric pressure. The effects of the temperature and the amount of supported photosensitizer on the ethylbenzene conversion and the ethylbenzene hydroperoxide selectivity and formation kinetic rate have been explored. Photochemically generated singlet oxygen is probably the active oxygen species in this oxidation reaction, although a thermal cleavage of the –O–O– bond of the ethylbenzene hydroperoxide present as a trace in the starting ethylbenzene should be also taken into account as a radical chain initiation mechanism. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ethylbenzene; Air photoxidation; Ethylbenzene hydroperoxide; Tungsten halogen lamp; Polymer supported Rose Bengal photosensitizer

1. Introduction

Propylene oxide is produced in the Repsol factory of Puertollano (Spain) by epoxidation of propylene with ethylbenzene hydroperoxide (EBHP), that is in turn produced by catalytic oxidation of ethylbenzene (EB) with air. The by-product of the epoxidation reaction, methyl phenyl carbinol, is later dehydrated to yield the monomer styrene. The global scheme is given in (Scheme 1).

In this paper we have focused our attention on the first step of this reaction scheme, the oxidation of EB to EBHP with air. This is a liquid-phase radical reaction, usually carried out at industrial level in reactors in series of about 50 m^3 of capacity. The conversion is usually kept at low levels, about 12% w/w EBHP in the reaction mixture (the maximum safe concentration of EBHP in EB is around 30% w/w), but the EBHP selectivity has to be very good, usually higher than 95% for a commercial application. The main reaction by-products are acetophenone (ACP), methyl phenyl carbinol (MPC) and phenol (PHE).

The slow atmospheric oxidation of a C–H bond to a C–O–O–H group (hydroperoxide) is called autoxidation. The reaction occurs when organic compounds are allowed to stand in air and is catalyzed by light, so that unwanted autoxidations can be greatly slowed by keeping the compounds in dark places. Oxygen itself (a diradical) is too unreactive to be the species that actually abstracts the hydrogen. But if a trace of a free radical (say $R'^{\bullet}$) is produced by some initiating process, it reacts with oxygen to give $R'–O–O^{\bullet}$ and this type of radical is capable of abstracting hydrogen and the radical chain reaction propagates. However, the reaction of activated hydrogen (allylic, benzylic,...) with oxygen that has been photosensitized yields the OOH substitution products in the allylic or benzylic positions [1]. The active oxygen species in this case is not the ground-state oxygen (a triplet) but an excited singlet state (in which all electrons are paired) [2,3] and the function of the photosensitizer is to promote the oxygen triplet to this singlet state. Electronically excited singlet-state oxygen is the reactive intermediate in the dye-sensitized photoxygentation of many organic compounds as demonstrated by comparison with the products obtained by reaction with singlet oxygen generated chemically [4]. In fact singlet oxygen can also be produced by non-photochemical means such as reaction between H_2O_2

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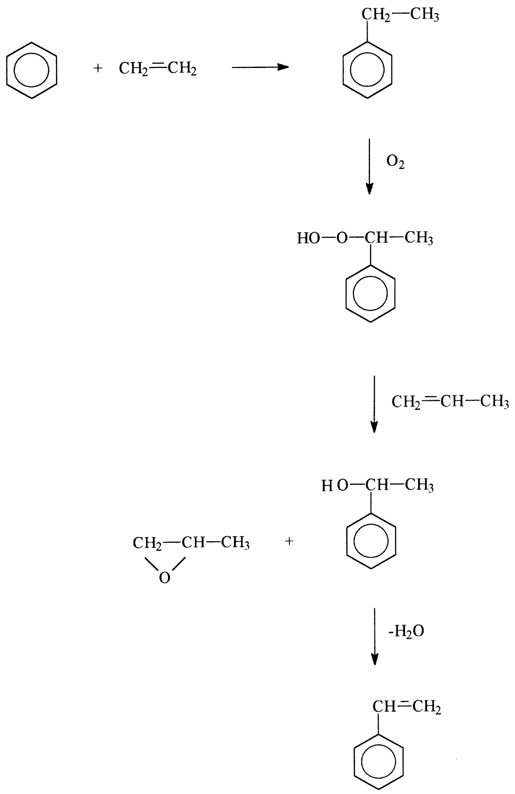


Scheme 1. Fabrication scheme of propylene oxide-styrene through ethylbenzene hydroperoxide.

and NaOCl [5] or between ozone and triphenylphosphite [6]. The singlet oxygen generated by either photochemical or non-photochemical methods reacts in the same way [7], and this is evidence that singlet oxygen is the reacting species in the photochemical reaction.

Singlet oxygen reacts with indoles towards dioxetanes and hydroperoxides as intermediates in dependence with the temperature: C_2–C_3 cleavage of the indole ring results at room temperature through a dioxetane while at −70°C only the hydroperoxide intermediate at the C_3 was detected [8–12].

Photoxidation of EB was carried out by irradiation of undiluted EB at 120°C with a 500 W tungsten halogen lamp. The generation of the singlet-state oxygen was made by means of Rose Bengal dye-sensitizer [13] supported on a basic anion exchange styrene-divinylbenzene resin (Lewattit M-500). The bulk EB was stirred at 1400 rpm and then air was bubbled through it, keeping dispersed the photosensitizing polymer.

2. Experimental

EB was oxidized with air at 120°C in a stirred tank reactor at atmospheric pressure, in the presence of a Rose Bengal photosensitizer supported on a styrene-divinylbenzene basic resin Lewattit M-500, irradiating with a 500 W tungsten halogen lamp.

2.1. Reaction equipment

The reactor was a 2 l round bottomed glass tank connected to a KPG type stirrer, a double jacket reflux condenser cooled by water, a type K thermocouple and a gas inlet system with a porous glass disk at the bottom. The KPG stirrer was powered by a variable speed (0–2000 rpm) engine Heidolph model RZR-2050. The reactor was surrounded by a heating mantle, controlled by a Proportional Integral Derivative (PID) temperature controller model TC-21 from the Instituto de Catálisis and Petroleoquímica (Madrid). The air was fed to the reactor from an air compressor Compact model Airblock-106 through a mass flow controller Brooks model 5850TR (0–1000 ml N/min±1%). This reactor was externally irradiated by a 500 W tungsten halogen lamp from Iwasaki Electric Co., Ltd.

2.2. Materials

EB was generously provided by Repsol S.A. from the ‘condensate F-255’ from its Puertollano plant and it contains 0.4% w/w of EBHP.

The polymer supported Rose Bengal photosensitizer was prepared according to the following experimental procedure: to a solution of 1 g of Rose Bengal in 50 ml of methanol, 5 g of commercial styrene-divinylbenzene resin Lewattit M-500 were added, and the mixture was vigorously stirred at room temperature for 1 h. The interchanged resin was then vacuum filtered, washed with methanol several times and later with water. The resin was vacuum dried to constant weigh; 5 g of resin fix around 0.6 g of dye (around 10% w/w of dye charged onto the resin).

Sodium iodide, glacial acetic acid, sodium thiosulphate, methanol and isopropanol were of analytical grade from Panreac. Triphenylphosphine was purchased from Fluka.

2.3. Reactor operation: general procedure

445 g of EB were charged into the reactor and the temperature controller and the agitation speed were set to the values designed for the experiment. 4.45 g of resin containing the photosensitizer were added to the reactor. When the temperature stabilized at the value previously set for the experiment, the air flow (60 l N/h) was set and kept constant during the experiment, and the tungsten lamp was switched on. Samples (about 10 ml) were taken from the reactor at regular intervals (typically 1 h) during the experiment, that lasted for about 8 h. At the end of the experiment, the resin was filtered off, washed with methanol and vacuum dried, making it ready for reuse.

2.4. Analysis

Determination of low levels of EBHP in EB has been carried out by near-infrared spectroscopy [14]. However, due to the range of EBHP contents of our samples, we had chosen a volumetric determination method. The weight per cent (% w/w) of EBHP in the samples taken from the reactor was determined by iodometric analysis, in the following way: 2 ml of glacial acetic acid were added to 25 ml of isopropanol in a 250 ml Erlenmeyer flask. Later, 10 ml of sodium iodide-isopropanol reagent (prepared by refluxing 22 g of sodium iodide in 100 ml of isopropanol, cooling and filtering) and around 1.5 g of the sample, in this order, were added. The mixture was refluxed gently for 5 min, and later 100 ml of distilled cold water were added through the reflux condenser. The samples, and the blank, were later titrated using 0.1 N sodium thiosulphate (previously standarized against potassium dichromate) until the yellow reddish colour of the iodine disappears. The EBHP % w/w was calculated from the formula.

$$\text{EBHP \% w/w} = \frac{(S - B) \times N \times F \times \text{MW} \times 100}{G \times 2000}$$

where S is the volume of sodium thiosulphate for the titration of the sample, B the volume of sodium thiosulphate for the titration of the blank, N is the normality of sodium thiosulphate, F is the factor of the sodium thiosulphate solution, MW is the molecular weight of EBHP and G is the sample weight.

The quantification of the reaction by-products, methyl phenyl carbinol (MPC), acetophenone (ACP) and phenol (PHE) was carried out by gas chromatography. The quantification method for MPC was based in the selective reaction of Triphenylphosphine with EBHP to give MPC and Triphenylphosphine oxide. The sample remaining from the EBHP determination (around 7.0 g) was cooled at 0°C, and the stoichiometric amount of Triphenylphosphine necessary to convert all EBHP to MPC was added. The vial was closed and shaken until the phosphine dissolved. This sample was injected (1 μl) in a GC Hewlett-Packard HP-5890 equipped with a capillary column CARBOWAX 20 M (25 m×0.25 mm×0.30 μm). The oven temperature was set at 60°C for 4 min, increased at 4°C/min to 200°C where it was kept for 3.5 min. The column head pressure was 35 kPa and the detector was a FID. This GC was calibrated for MPC, ACP and PHE, and the concentrations of ACP and PHE could be determined directly from the calibration curves. Once determined the concentrations of EBHP (by titration) and MPC (by chromatography), the concentration of MPC in the reactor sample could be calculated by the difference between the MPC concentration obtained by GC and the EBHP concentration (in mol/l) obtained by titration.

Some GC samples were reanalyzed by gas chromatography/mass spectrometry (GC/MS) in order to identify trace components. Samples were injected in a GC/MS Hewlett-Packard GC 6890/MSD 5359, equipped with a capillary column Alltech AT-5 (25 m×0.25 mm×0.20 μm). The oven temperature was kept at 60°C for 1 min, and raised at 6°C/min to 300°C where it was kept for 10 min. The injector was set to splitless mode, and we injected 4.0 μl. The mass spectra were registered under electron impact at 70 eV, ion source 230°C, scanning from 35 to 550 Dalton. The mass spectra of the trace compounds found in the samples were matched with the spectra from the Wiley 275 Database using the software ChemStations. The main trace components we have found were.

- 2-phenylethanol, *o*-ethylphenol *m*-ethylphenol and α-hydroxyacetophenone, as the result of the oxidation of EB at positions different from the benzylic position.
- oxidation products of the impurities in the EB: 1-phenyl-1-propanol from the oxidation of *n*-propylbenzene, *o*-methyl benzyl alcohol from the oxidation of *o*-xilene, α-isopropyl benzyl alcohol from the oxidation of isobutylbenzene and *p*-isopropyl benzyl alcohol from the oxidation of *p*-methylcumene.
- products of the termination reaction by radical coupling: *erythro* and *threo*-2,3-diphenylbutane, as the result of the coupling of two α-phenyl ethyl radicals, and *erythro* and *threo*-α-methyl benzyl ether, as the result of the coupling of a α-phenyl ethyl radical with a α-phenyl ethoxyl radical.

The oxygen concentration in the effluent air from the reactor was determined by gas chromatography in GC Hewlett-Packard 5840, using a packed column Carbosieve SII (10′×1/8′ SS) and a TCD detector. The mean oxygen concentration found in the effluent air in all experiments was 16% v/v.

2.5. Definitions

Ethylbenzene conversion was defined as

$$\text{EB Conversion (\%)} = \frac{[\text{EBHP}] + [\text{MPC}] + [\text{ACP}] + [\text{PHE}]}{[\text{EB}]_0} \times 100$$

where [EBHP], [MPC], [ACP] and [PHE] were the molar concentrations of ethylbenzenehydroperoxide, methylphenylcarbinol, acetophenone and phenol, respectively, in the sample and $[\text{EB}]_0$ was the initial molar concentration of ethylbenzene (8.166 M).

EBHP selectivity was defined as

$$\text{EBHP Selectivity (\%)} = \frac{[\text{EBHP}]}{[\text{EBHP}] + [\text{MPC}] + [\text{ACP}] + [\text{PHE}]} \times 100$$

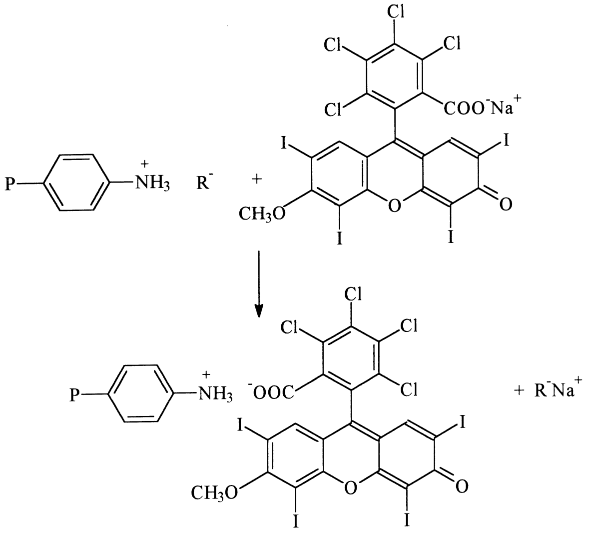
where the acronyms between square brackets have the same meaning as in the precedent paragraph.

3. Results and discussion

The ionic anchorage of the Rose Bengal dye to the resin was carried out easily stirring the resin in a methanolic solution of the dye at room temperature (Scheme 2). The yields in the photoxidative cleavage of indoles increase with the supported photosensitizing in 30% on the same reaction using the unsupported one [9,10], and the separation and regeneration of the resin supported photosensitizer are very straightforward. Moreover, the presence of trace amounts of any catalyst is undesirable in the second step (see Scheme 1) of this petrochemical pathway to propylene oxide-styrene [15], which is avoided by the use of polymer supported photosensitizer.

However, the EB that we use as raw material in our photoxidation experiments is an industrial product (condensate F-255) that contains about 0.4% w/w of EBHP. Moreover, any EB without radical inhibitor added would contain always trace amounts of EBHP due to autoxidation. Thus a thermal cleavage of the –O–O– bond of EBHP should be taken into account working at 120°C , and the radicals formed can act as chain radical initiators abstracting hydrogen form the EB.

This was an important concern at the beginning of our experiments on photoxidation of EB, and we ran two experiments, one with irradiation and photosensitization and the other without any of them, keeping constant the rest of the operating variables of the reactor (temperature, stirring speed, air flow, reactor tank,...). Fig. 1 (a) shows the EBHP % w/w versus time (min) for both experiments: clearly, the kinetic rate of EBHP formation (w_{EBHP}) is much better for the photochemical experiment ($w_{\mathrm{EBHP}}=1.3\times10^{-5}\,\mathrm{mol\,l^{-1}\,s^{-1}}$) than for the experiment without photocatalysis ($w_{\mathrm{EBHP}}=8.0\times10^{-6}\,\mathrm{mol\,l^{-1}\,s^{-1}}$) (Table 1). If we compare the plots of EBHP selectivity versus EBHP conversion for these two experiments (Fig. 1b), we could observe that at low conversions, the selectivity is better for the experiments without irradiation but at higher conversions the experiment with irradiation yields better selectivity with an increasing trend. From these results, it is clear that two different chain initiation mechanisms are operating in our experiments: (a) a thermal cleavage of the –O–O– bond of the hydroperoxide present in the starting EB and (b) an activation of the oxygen molecule as singlet oxygen by the photosensitization.



Scheme 2. Anchorage of Rose Bengal dye to the styrene-divinylbenzene basic resin Lewattit M-500.

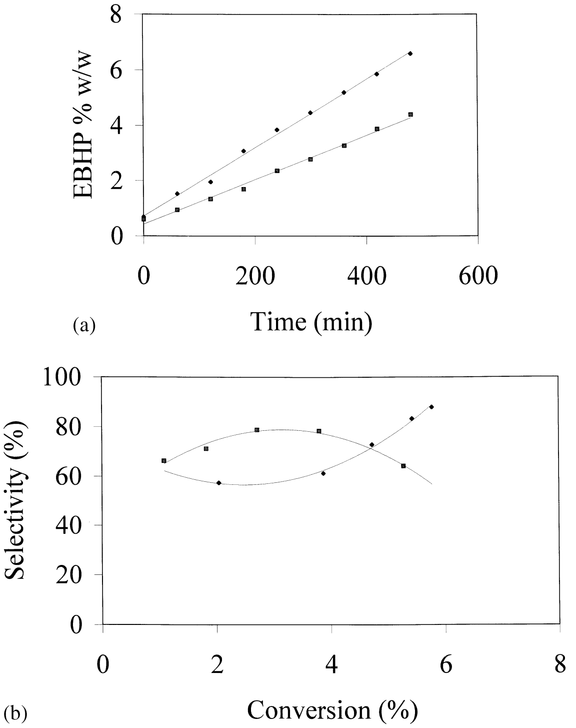


Fig. 1. (a) Kinetic plot of EBHP % w/w vs. time (min) and (b) EBHP selectivity (%) vs. EB conversion (%) for the experiments without irradiation (■) and with irradiation (500 W tungsten halogen lamp) and 1% w/w resin (◆). Temperature, 120°C. Stirring speed, 1400 rpm.

The overall radical chain mechanism of the air photoxidation of EB can be outlined as follows:

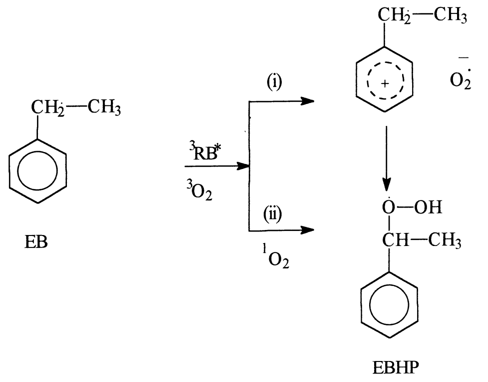
$$\text{Initiation}\quad {}^3\mathrm{RB}^* + {}^3\mathrm{O}_2 \xrightarrow{k_i} [\mathrm{RB}\cdots\mathrm{O}_2] \rightarrow \mathrm{RB} + {}^1\mathrm{O}_2$$

$$\mathrm{RH} + {}^1\mathrm{O}_2 \rightarrow \mathrm{R}^\bullet + {}^\bullet\mathrm{OOH}$$

Table 1
Kinetic rates of EBHP formation in $\mathrm{mol\,l^{-1}\,s^{-1}}$ (w_{EBHP})

Temperature (°C)	Resin (% w/w)	$W_{\mathrm{EBHP}}\times10^{-5}(\mathrm{mol\,l^{-1}\,s^{-1}})$
120	1	1.30
110	1	0.53
100	1	0.21
120	2	1.06
120	0	1.01
120	(*)[a]	0.80

[a] Without irradiation nor resin.



Scheme 3. Proposed mechanisms of EB photoxidation, RB=Rose Bengal.

$R^\bullet + O_2 \rightarrow RO_2^\bullet$

RB = Rose *Bengal*

Propagation $RO_2^\bullet + RH \xrightarrow{k_p} \underset{\text{(EBHP)}}{RO_2H} + R^\bullet$

$R^\bullet + O_2 \rightarrow RO_2^\bullet$

Termination $RO_2^\bullet + RO_2^\bullet \xrightarrow{k_t}$ Coupling by-product

An alternative proposal has been given to explain the photoxidation of aromatic compounds at benzylic positions; in this proposal, two mechanisms should be operating simultaneously: (i) the formation of a radical-ion pair with superoxide anion as a consequence of the sensitization, and (ii) the formation of singlet oxygen as the active oxygen species (see mechanism above). Both mechanisms are summarised in (Scheme 3) for EB [16,17].

3.1. Effect of the temperature

We tried to keep at a minimum level the thermal initiation process lowering the temperature, since we thought that this thermal process should be more sensible to the temperature than the photochemical one, with a view to improve the selectivity of the whole process as singlet oxygen shows special selectivity for hydrogen abstraction at benzylic positions, whereas the thermally formed radical should be less selective. Thus we ran experiments with irradiation and photosensitization at 120, 110 and 100°C (120°C was the maximum operating temperature of the Lewattit resin). Fig. 2(a) shows the kinetic plots of EBHP % w/w versus time (min) for the three temperatures: the effect of the temperature is very important, and the EBHP formation kinetic rate drops dramatically as the temperature lowers (Table 1). By plotting the EBHP formation kinetic rate ($mol\,l^{-1}\,s^{-1}$) versus 1/T (K^{-1}) we have found an activation energy of 111.04 $kJ\,mol^{-1}$ for the oxidation reaction in these conditions (R^2=1.0000). The effect of the temperature on the EBHP selectivity could be observed in the Fig. 2(b): at 100°C we have low selectivity at low conversions; by rising the temperature at 110°C we improve the conversion but lowering the selectivity, and a further rise of the temperature to 120°C improves the selectivity keeping the same levels of conversion. Thus, we did not succeeded in to improve the selectivity by lowering the temperature since the kinetic rate constant of the benzylic photoxidation reaction is probably more sensible to the effect of the temperature than the rate constants of the side reactions.

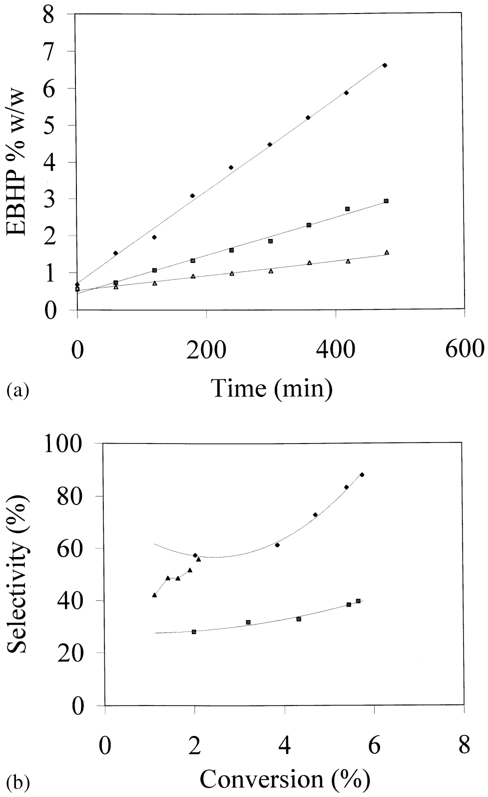


Fig. 2. (a) Kinetic plot of EBHP % w/w vs. time (min) and (b) EBHP selectivity (%) vs. EB conversion (%) for three temperatures, 120°C (◆), 110°C (■) and 100°C (▲). Stirring speed, 1400 rpm.

3.2. Effect of the concentration of polymer supported Rose Bengal photosensitizer

The effect of the amount of polymer supported Rose Bengal photosensitizer on the kinetic rate and selectivity of EBHP formation is shown in Fig. 3(a) and (b). The three experiments were carried out under the same conditions, irradiating externally with the tungsten halogen lamp and using 0, 1 and 2% (w/w) of the resin, respectively. The experiments with and without photosensitizer show roughly the same kinetic plots, only the experiment carried out with 1% w/w photosensitizer gives a slightly better kinetic rate (Table 1). The main differences are observed with the selectivity that is much better in the experiments done with photosensitizer. Light itself (as we have mentioned earlier) catalyzes

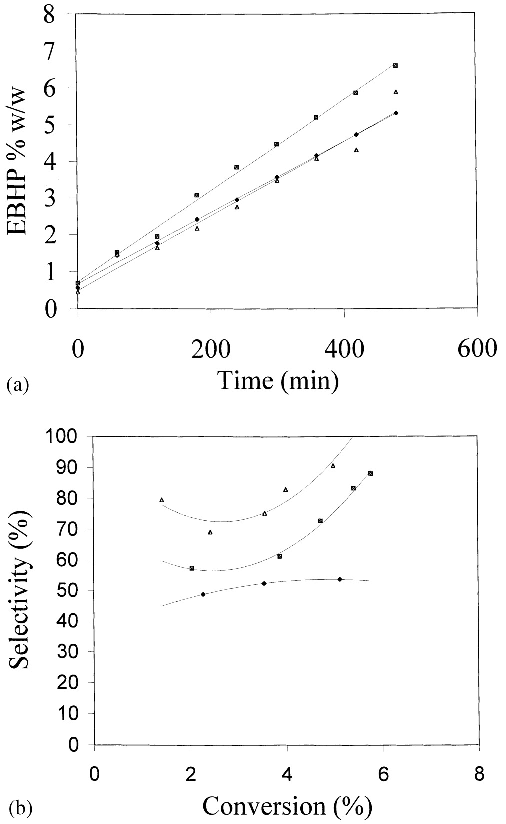


Fig. 3. (a) Kinetic plot of EBHP % w/w vs. time (min) and (b) EBHP selectivity (%) vs. EB conversion (%) for three concentration of resin supported photosensitizer, 0% w/w (◆), 1% w/w (■) and 2% w/w(▲). Temperature, 120°C. Stirring speed, 1400 rpm.

the oxidation of EB, but the reaction is more selective in the presence of Rose Bengal since more singlet oxygen would be present in the reaction medium and this activated oxygen molecule would abstract preferentially the benzylic hydrogen of EB, directing the photoxidation towards the desired EBHP product.

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