

Epoxidation of Styrene to Styrene Oxide: Synergism of Heteropoly Acid and Phase-Transfer Catalyst under Ishii–Venturello Mechanism

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Abstract:

Epoxidation of olefinic double bonds is of considerable importance in a variety of industries. Epoxides are raw materials for a wide variety of chemicals such as glycols, alcohols, carbonyl compounds, alkanolamines, and polymers such as polyesters, polyurethanes, and epoxy resins. Epoxidation of styrene with aqueous H_2O_2 was carried out by using synergism of heteropoly acids and phase-transfer catalysis in a biphasic system under the so-called Ishii–Venturello chemistry. The kinetics of epoxidation of styrene to styrene oxide was studied. Styrene was converted quantitatively to styrene oxide with 100% selectivity of the converted styrene in ethylene dichloride as the solvent at 50 °C. The effects of various parameters were studied on the rate of reaction. Dodecatungstophosphoric acid (DTPA) and cetyldimethylbenzylammonium chloride (CDBAC) were found to be the best heteropoly acid (HPA) and PTC combination, respectively, for the epoxidation. The reaction mechanism is very complex. At higher temperatures, there is a slight degradation of hydrogen peroxide as well as some thermal oligomerisation of styrene. The kinetic equation is complex due to the nature of the epoxidising species. The reaction can be represented by a pseudo-first-order kinetics where the order in styrene concentration is unity. An apparent activation energy of 7.26 kcal/mol was found.

Introduction

Styrene oxide is an important intermediate in organic process industry, and it can be produced by epoxidation of styrene amongst other routes. The current work was centered around the epoxidation of styrene to styrene oxide by using a synergism of heteropoly acids and phase-transfer catalysts under the so-called Ishii–Venturello chemistry.

There are several methods of preparation of epoxides, starting from olefins, α -halocarbonyls, carbonyls, epichlorohydrin, and substituted hydroxyl compounds.^{1–3} Epoxidation with commercially available peroxyacids such as peroxyacetic acid, peroxybenzoic acid, peroxyfluoroacetic acid, *m*-chloroperoxybenzoic acid, and *m*-nitroperoxybenzoic acid is often a method of choice for laboratory preparation. However, peroxy acids are hazardous to handle and the yields obtained by using them in the epoxidation of some industrially relevant compounds such as α -olefins are poor. On the

other hand, organic hydroperoxides such as cumene hydroperoxide (CHP), *tert*-butyl hydroperoxide (TBHP), ethylbenzene hydroperoxides (EBHP), etc.^{1,4} possess many advantages, including relative ease of handling and their higher reactivities. Acid labile epoxides of such compounds as styrene, α -methylstyrene, α -pinene, etc. which cannot be prepared with peroxy acids have been prepared in excellent yield by using hydroperoxides.

A practical route for direct epoxidation of olefins by aqueous H_2O_2 which is environmentally clean and relatively easy to handle, through the use of a suitable catalyst, is desirable.⁵ The synergism of phase-transfer catalysis and tungstate and phosphate (arsenate) ions under acidic conditions or heteropoly acids for the oxidation of olefins, alcohols, and diols with dilute H_2O_2 has been achieved in the laboratories of Ishii⁶ and Venturello^{7,8} who have demonstrated that olefins can be epoxidized with dilute H_2O_2 (<10%) with high selectivity to epoxide (80–90%) in short times under mild conditions. These are now called Ishii–Venturello epoxidations.

Heteropolyacids (HPA), such as dodecatungstophosphoric acid and dodecamolybdophosphoric acid are often used not only for the oxidation of organic substrates but also for many acid-catalyzed reactions because they possess the dual characteristics of oxidising ability and strong acidity. The use of HPA for the oxidation of olefins with H_2O_2 generally produces trans glycols because of the subsequent cleavage of the oxirane ring of the reacting epoxide by electrophilic attack of strong acid. However, with the PTC, the epoxides are easily formed under milder conditions.

Ishii–Venturello Epoxidation. In the context of epoxidation of styrene, it is appropriate to deal briefly with the Ishii–Venturello chemistry that involves the use of HPA, H_2O_2 , and PTC, which was useful in the interpretation of rate data in the present studies.

The highly selective epoxidation of terminal alkenes by the complex $\text{W}^{\text{VI}}/\text{P}^{\text{V}}/\text{H}_2\text{O}_2/\text{PTC}$ has been extensively investigated by several groups and was recently commercialised.⁹ There are contradictory reports about the basic mechanism, and two schools of thought have emerged. According to the general concept of PTC, various steps in this system are given

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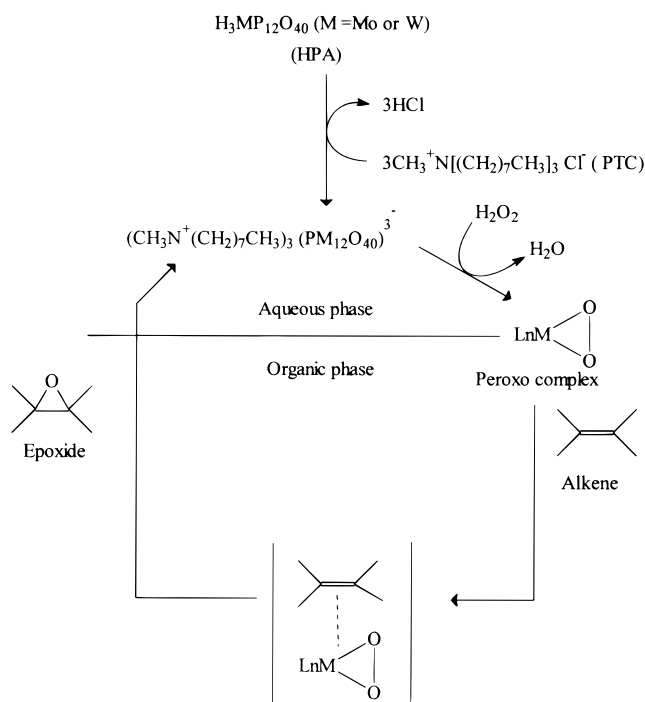
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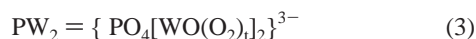
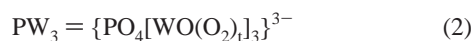
Scheme 1



in Scheme 1 as proposed by Ishii's group.

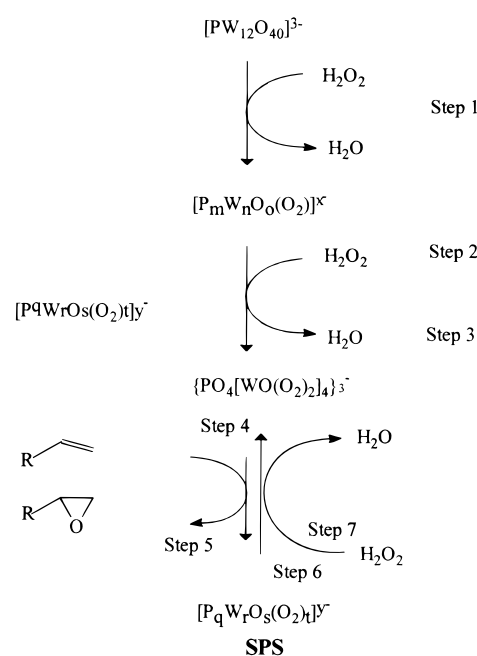
On the other hand, Duncan et al.⁹ have thoroughly investigated 1-octene conversions and 1,2-epoxyoctane selectivities under biphasic conditions: H_2O_2 /1-octene in CHCl_3 , with 21 different polyoxometalates and cetylpyridinium chloride as the PTC, including the Ishii precursor complex $[\text{PW}_{12}\text{O}_{40}]^{3-}$. In this work, it was established that only $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and $[\text{PW}_{11}\text{O}_{39}]^{3-}$, which rapidly form the polyperoxometalate $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, are the effective species. Further, the only significant side reaction is H_2O_2 disproportionation to water and O_2 at 60 °C. The structure of this complex polyperoxophosphotungstate (ES) is given in Scheme 2. Kinetic and spectroscopic studies have shown that both PW_4 and PW_3 species are formed initially, and one PW_2 species subsequently, in the reaction. Here, PW_n ($n = 2, 3, 4$) stands for PW_nO_x , and these are called subsequent peroxo species (SPS). Yadav and Satoskar¹⁰ developed kinetic expressions for the Ishii–Venturello epoxidation.

Duncan et al.,⁴ have not given any direct structure of any of the species PW_4 , PW_3 , and PW_2 except the comment that these species are capable of coordinating with quaternary cation Q^+ . Further, in the case of PW_4 , it is expected that three of the tungsten sites remain seven-coordinated and the fourth does not, meaning that the latter must find a ligand in the reaction mixture to obtain coordinate saturation. It was inferred in our earlier work⁵ that the PW_4 and PW_3 SPS are likely to be



The value of t is most probably 1. These are all represented by $\{\text{P}_q\text{W}_r\text{O}_s(\text{O}_2)_t\}^{y-}$. The most important infer-

Scheme 2



ence which can be drawn from the current work is that the quaternary salt of all SPS species is Q_3SPS and mainly Q_3PW_4 because PW_4 is the dominant species.

The polytungstophosphate formation depends on the ratio $[\text{H}_2\text{O}_2]/\{\text{H}_3[\text{PW}_{12}\text{O}_{40}]\}$. Addition of H_2O_2 to the HPA solution leads to formation of a number of unidentified species, and at least 50 equiv of H_2O_2 are required to form the epoxidizing species $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, which is designated as ES.

In the epoxidation reaction, the quaternary salt of the epoxidizing species ES requires 1 equiv of olefin. The quaternary salt Q_3ES contains 8 equiv of peroxide. The species formed upon transfer of 1 equiv of active oxygen is likely to be not only epoxidation competent but also optionally situated to regenerate Q_3ES in the presence of H_2O_2 . The reaction of terminal olefin with Q_3ES produces the epoxide and the quaternary salts of the inorganic species PW_4 , PW_3 , and PW_2 . As said earlier, these are called the “subsequent peroxo species” (SPS) in the form of Q_3SPS . Q_3SPS reacts with 1 equiv of H_2O_2 to partially regenerate Q_3ES and 50 equiv of H_2O_2 to completely regenerate Q_3ES .

The coordination number of W is 5 (distorted pentagonal bipyramidal) in ES, and also probably in SPS. Both PW_4 and PW_3 species are formed upon transfer of oxygen from ES to olefin. Thus, the value of r in the SPS formula $[\text{P}_q\text{W}_r\text{O}_s(\text{O}_2)_t]^{y-}$ is primarily 4 or 3 and to a lesser extent 2. SPS PW_4 , PW_3 and PW_2 readily convert back to ES under turnover conditions (i.e., biphasic with aqueous H_2O_2 present), and ES is by far the dominant polytungstophosphate present under such conditions. The necessary implication is that the reoxygenation of PW_4 , PW_3 , and PW_2 by H_2O_2 is faster than epoxidation by ES.

The exact stoichiometry of transformation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ into the epoxidizing species ES, $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ in the presence of H_2O_2 is not precisely known. However, it is

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mentioned that the molar ratio of H_2O_2 and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is very important and that at least 25 equiv of H_2O_2 are required to form $\text{Q}_3^+[\text{ES}]^{3-}$. It is therefore necessary to use a large excess of H_2O_2 over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in reaction with α -olefins. The current work followed the same principle for epoxidation of styrene.

Thus, the rate of epoxidation is derived by Yadav and Satoskar¹⁰

$$r_E = k_{\text{app}} C_{\text{A,org}} [\text{Q}_{\text{aq}}]^\alpha [\text{HPA}]^\beta [\text{H}_2\text{O}_2]^\gamma \quad (4)$$

where k_{app} is the apparent rate constant and α, β, γ are orders of reaction, and Q_{aq} is the total quantity of quaternary added initially to the aqueous phase:

Since for a typical experiment the concentrations of the PT catalyst, HPA, and H_2O_2 were held constant, the above equation can be integrated to get the following:

$$-\ln(1 - X_A) = k_1 t \quad (5)$$

where

$$k_1 = k_{\text{app}} [\text{Q}_{\text{aq}}]^\alpha [\text{HPA}]^\beta [\text{H}_2\text{O}_2]^\gamma \quad (6)$$

Studies have been conducted with phase-transfer catalysed epoxidation in the presence of heteropoly acids for α -olefins such as 1-octene by Duncan et al.,⁹ and for alkyl undecylinates and undecylinic acid by ourselves.¹⁰ The current work addresses the epoxidation of styrene, including kinetic modeling.

Experimental Section

Catalysts and Chemicals. Tricaprylmethylammonium chloride (Aliquat 336) (AR grade) was obtained from SISCO Laboratories, Mumbai, India. Ethyltriphenylphosphonium bromide (ETPPB), tetrabutylammonium bromide (TBAB), cetyldimethylbenzylammonium chloride (CDBMAC), and Aracad (Cetyltrimethylammonium chloride) were obtained from Dishman Pharmaceuticals and Chemicals, Ahmedabad, India. Dodecatungstophosphoric acid (DTPA) (AR grade), dodecaphosphomolybdic acid (DPMA), and hydrogen peroxide 30% w/v, (AR grade) were obtained from s.d.Fine Chemicals Ltd, Mumbai, India. Styrene was obtained from Herdillia Chemicals Ltd, Mumbai, India.

Reaction Procedure. The reactor consisted of a flat-bottom glass vessel of 5 cm i.d. and 150 mL capacity equipped with four baffles, a turbine stirrer, and a reflux condenser. The assembly was kept in an isothermal oil bath at a constant known temperature and mechanically agitated with an electric motor. A typical reaction mixture consisted of 0.2 mol styrene with 15 mL of ethylene chloride and 15 mL of 30% hydrogen peroxide (0.132 mol) with 1 g of PTC and 1.5 g of HPA. A pH of 4.0 was adjusted by adding a dilute sodium hydroxide solution. The reaction was typically carried out at 50 °C at a stirrer speed of 800 rpm.

Analysis and Identification of Product. Samples were withdrawn periodically, and the analysis was performed by gas chromatography (Chemito model 8510) by using a 2 m \times 3.25 mm i.d. stainless steel column packed with 5% OV-

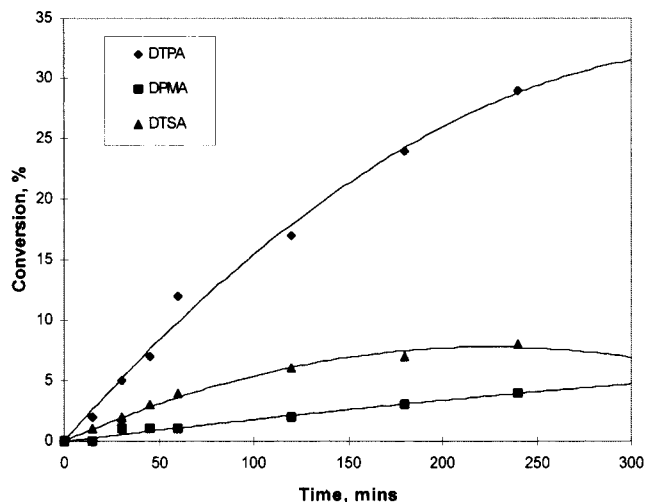


Figure 1. Effect of different HPAs. Styrene: 0.2 mol. PTC (cetyldimethylbenzylammonium chloride): 0.0023 mol. H_2O_2 : 15 mL. HPA loading: 3% w/w. Speed of agitation: 800 rpm. Temperature: 50 °C.

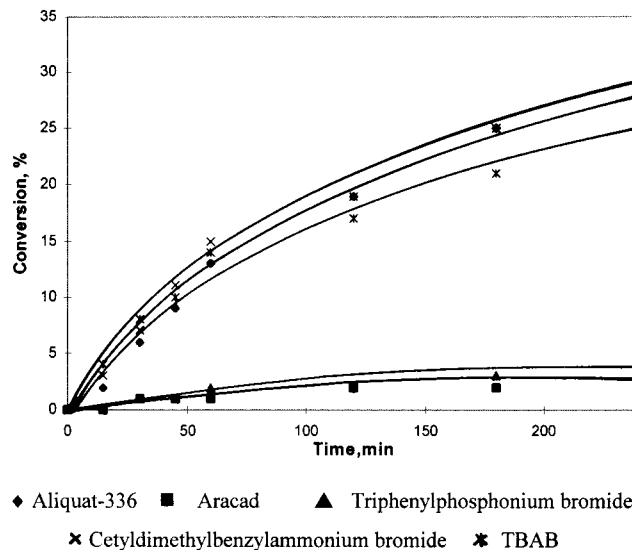


Figure 2. Effect of different PTCs. Styrene: 0.2 mol. PTC: 0.0023 mol. H_2O_2 : 15 mL. Catalyst loading: 3% w/w. Catalyst: DTPA. Speed of agitation: 800 rpm. Temperature: 50 °C.

17 on Chromosorb WHP coupled with a flame ionisation detector. Quantitative analysis was done by using synthetic mixture. Typical GC-MS analysis was also done to ascertain the products.

As will be explained later, H_2O_2 was used sub-stoichiometrically, and the conversions are based on it. The selectivity to styrene oxide was found to be 100%. Beyond 60 °C, hydrogen peroxide starts decomposing, and thermal oligomerisation of styrene sets in; hence, all experiments were done at 50 °C. Hydrogen peroxide efficiency was almost 100% at low temperatures. In semi-batch mode of operation hydrogen peroxide was added dropwise to the reaction mixture to avoid any decomposition. The reaction mixture is typically washed with water to remove the unreacted H_2O_2 , HPA, and PTC, and the organic phase is distilled under vacuum.

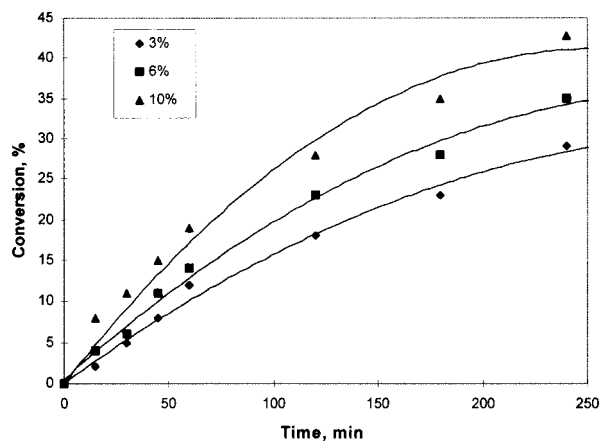


Figure 3. Effect of DTPA concentration. Styrene: 0.2 mol. PTC (cetyldimethylbenzylammonium chloride): 0.0023 mol. H_2O_2 : 15 mL. Speed of agitation: 800 rpm. Temperature: 50 °C.

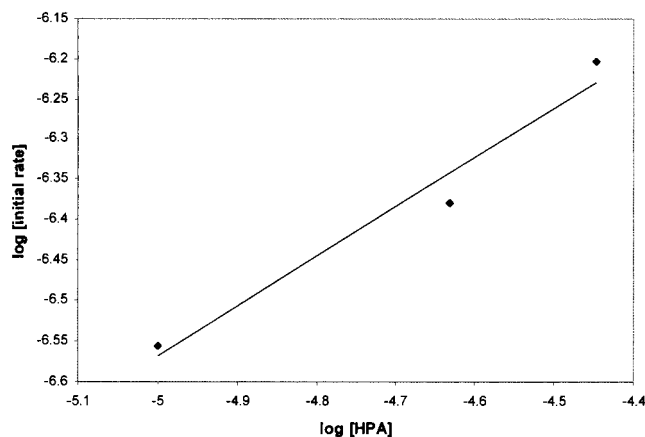


Figure 4. Plot of log[initial rate] vs log[HPA].

Results and Discussion

Effect of Different Heteropoly Acids. Since the concentration and partitioning of the epoxidising species are functions of the heteroatom in the heteropoly acid, it was thought worthwhile to study the effect of the type of heteropoly acid on the epoxidation of styrene. The efficacy of different heteropoly acid catalysts was evaluated at 50 °C under otherwise similar conditions in the absence of any mass transfer resistance. The catalysts used were dodecatungstophosphoric acid (DTPA), dodecaphosphomolybdic acid (DPMA), and dodecatungstosilicic acid (DTSA).

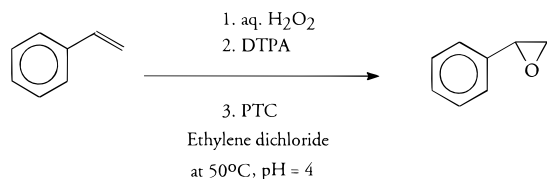


Figure 1 shows that DTPA was the best heteropolyacid giving very high conversions. The concentration of the epoxidising species in the organic phase also depends on the quaternary cation Q^+ . In further experiments, DTPA was used as the heteropolyacid in conjunction with other PTC.

Effect of structure of PTC. Four different phase-transfer catalysts (PTC) were used to find out the best HPA–PTC combination (Figure 2). The choice of the catalysts was based

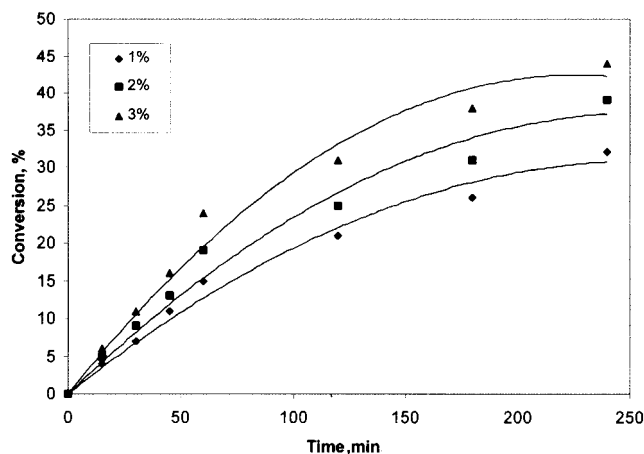


Figure 5. Effect of PTC concentration. Styrene: 0.2 mol. PTC (cetyldimethylbenzylammonium chloride): H_2O_2 : 15 mL. Catalyst loading: 3% w/w. Catalyst: DTPA. Speed of agitation: 800 rpm. Temperature: 50 °C.

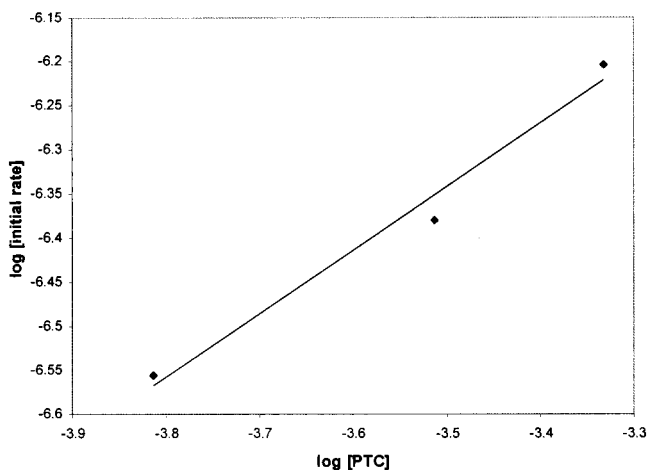


Figure 6. Plot of log[initial rate] vs log [PTC].

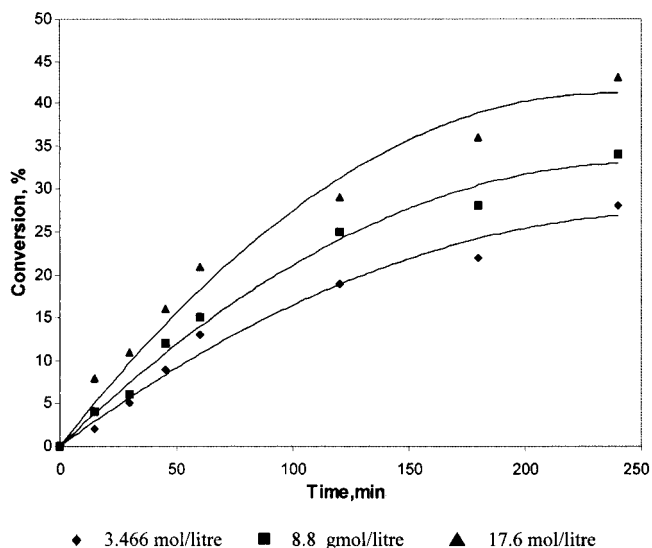


Figure 7. Effect of H_2O_2 loading. Styrene: 0.2 mol. PTC (cetyldimethylbenzylammonium chloride): 0.0023 mol. Catalyst loading: 3% w/w. Catalyst: DTPA. Speed of agitation: 800 rpm. Temperature: 50 °C.

on their stability in the presence of HPA, easy availability, and possible efficiency in the formation of the peroxo

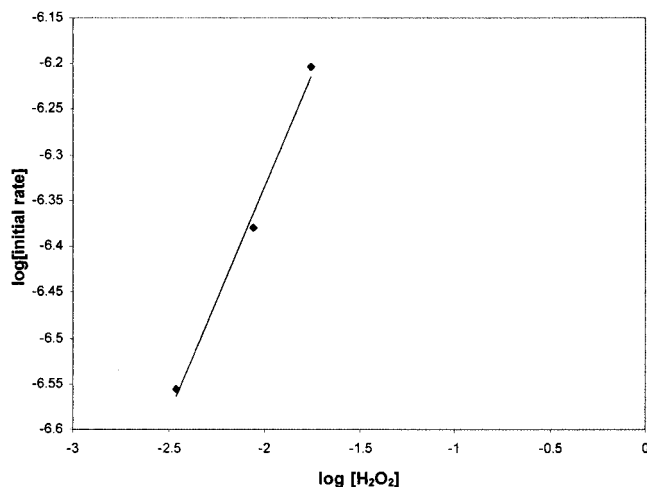


Figure 8. Plot of log[initial rate] vs log[H₂O₂].

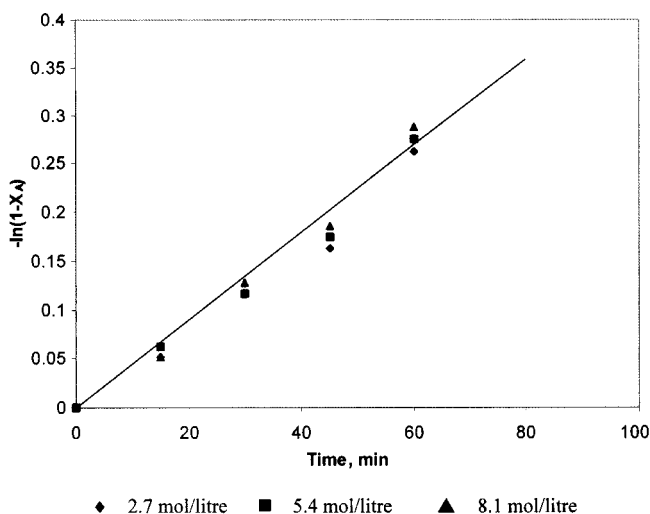


Figure 9. Typical pseudo-first-order plot. PTC (cetyldimethylbenzylammonium chloride): 0.0023 mol. Catalyst loading: 3% w/w. Catalyst: DTPA. Speed of agitation: 800 rpm. Temperature: 50 °C.

complex. It was found that CDMBAC offered the best yields at low concentrations in comparison with others. The efficacy of the PTC was found to be in the order: CDMBAC > TBAB > Aliquat-336 > ETPPB > Aracad.

CDMBAC provides the best accessibility parameter defined as $q (= 1/16 + 1/1 + 1/1 + 1/7 = 2.205)$ and is unsymmetrical and tends to reside at the interfacial region,^{11,12} and therefore, its ion-pair with the peroxy species is more readily available for the oxidation reaction in comparison with others.

Therefore, DTPA and CDMBAC were chosen for further experimentation.

Effect of DTPA Concentration. After it was ascertained that DTPA and CDMBAC pair was found to give the best results, the effect of the concentration of DTPA was studied under otherwise similar conditions (Figure 3). It was observed that the conversion increases with concentration of DTPA. A plot of initial rate of reaction against DTPA

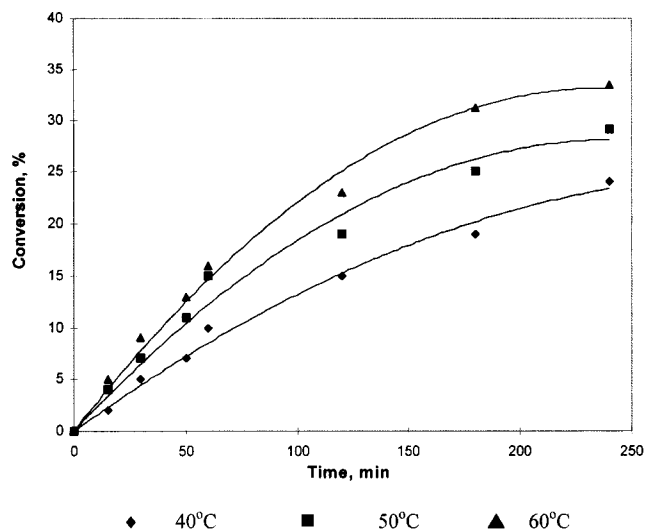


Figure 10. Effect of temperature. Styrene: 0.2 mol. PTC (cetyldimethylbenzylammonium chloride): 0.0023 mol. Catalyst loading: 3% w/w. Catalyst: DTPA. Speed of agitation: 800 rpm.

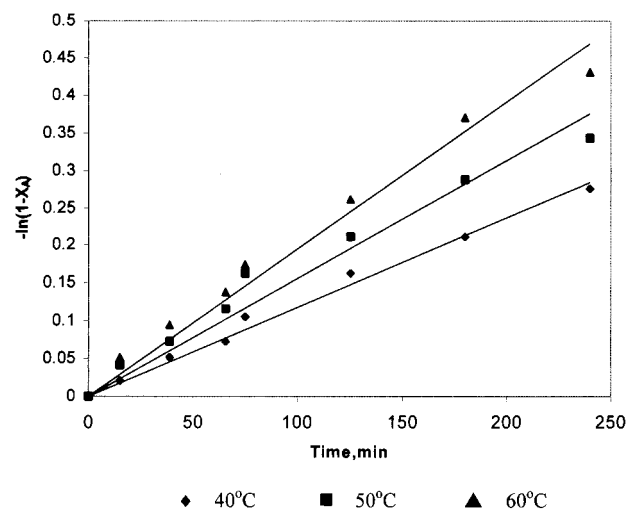


Figure 11. Plot of $-\ln(1 - X_A)$ vs time at different temperatures.

concentration on a log-log plot was made to get the order of reaction in DTPA concentration, β , according to eq 4. (Figure 4). From this β was found as 0.62.

Effect of PTC Concentration. The effect of concentration of phase-transfer catalyst on epoxidation rate was studied (Figure 5). The conversions were found to increase with increasing PTC concentrations. Initial rates of reaction were plotted against concentration of catalyst on a log-log scale in Figure 6. The slope of the plot (γ) is 0.72 which is the order in the catalyst concentration as per eq 4.

Effect of H₂O₂ Loading. The effect of concentration of H₂O₂ was studied in the range of 3.466 to 17.6 mol/L of aqueous phase (Figure 7). The plot of log [initial rates] against log[H₂O₂] is shown Figure 8. To find the reaction order in H₂O₂ as 0.5.

Effect of Styrene Concentration. The reaction was carried out at three different concentrations. Typical first-order plots of $-\ln(1 - X_A)$ vs t as per eq 5 are given in Figure 9 at three different initial concentration of styrene. The slope of this line is $k_1 = 0.0027 \text{ min}^{-1}$, which is the

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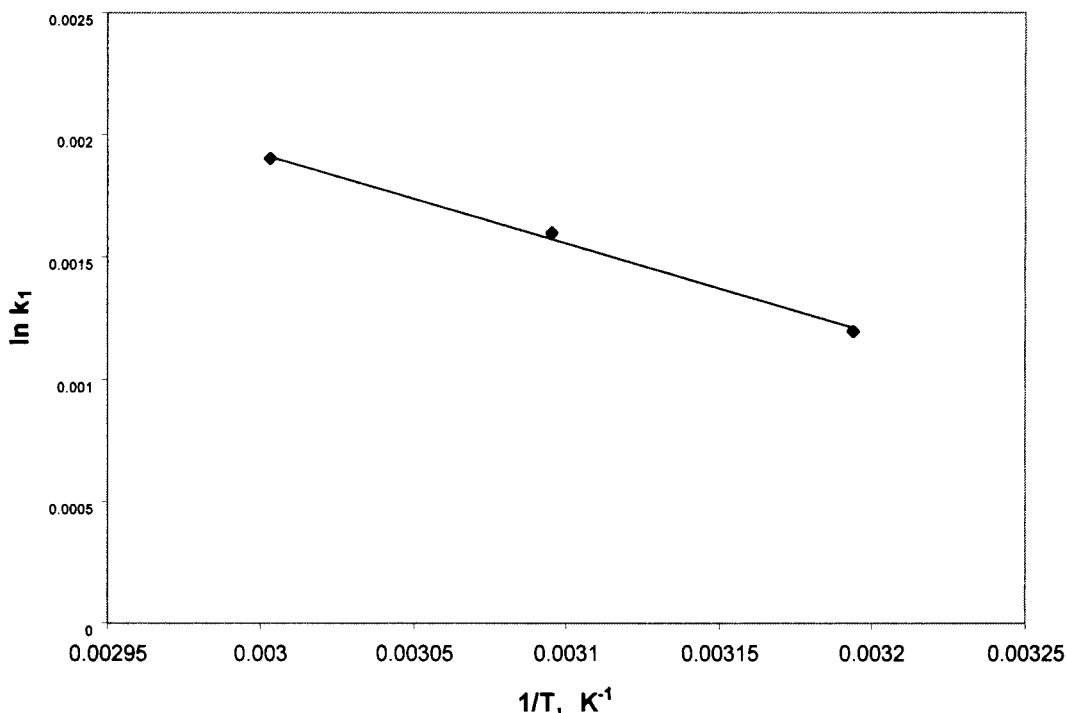


Figure 12. Arrhenius plot.

pseudo-first-order constant at 50 °C.

Effect of Temperature. The reaction was studied at three different temperatures in the range of 40–60 °C (Figure 10). At higher temperatures beyond 60 °C, there is a slight degradation of hydrogen peroxide as well thermal oligomerisation of styrene. The conversion was found to increase substantially with increasing temperature. Once again, the typical pseudo-first-order plots were made at different temperatures giving three pseudo-first-order constants k_1 (Figure 11). Arrhenius plots were made in Figure 12 of $\ln k_1$ against T^{-1} to get an activation energy of 7.26 kcal/mol. This value suggests that the reaction is kinetically controlled.

Kinetic Expression. The above analysis leads to the following rate of epoxidation of styrene:

$$r_E = k_{\text{app}} C_{\text{Aorg}} [Q]^{0.72} [\text{DTPA}]^{0.62} [\text{H}_2\text{O}_2]^{0.5} \quad (7)$$

A few comments are in order on these kinetics. Except the order of unity in styrene concentration, the orders in other species are fractional, suggesting a very complex mechanism. As has been shown in the earlier paper from this laboratory,¹⁰ the concentration of the epoxidising species $Q_3\text{ES}$ is governed by those of DTPA, H_2O_2 , and Q^+X^- which are related through a complex equilibria and stoichiometry, and hence it results in fractional orders.

Conclusions

Epoxidation of styrene to styrene oxide was studied by using a synergism of phase-transfer catalysis and heteropoly

acids using hydrogen peroxide as the oxidant. Styrene is converted quantitatively to styrene oxide with 100% selectivity of the converted styrene in ethylene dichloride as the solvent at 50 °C. Dodecatungstophosphoric acid (DTPA) and cetyldimethylbenzylammonium chloride (CDMBAC) were found to be the best heteropoly acid (HPA) and PTC combination, respectively for the epoxidation. The reaction mechanism is very complex. At higher temperatures, there is a slight degradation of hydrogen peroxide as well as thermal oligomerisation of styrene. The kinetic expression is complex due to the nature of the epoxidising species whose concentration is governed by those of DTPA, H_2O_2 , and Q^+X^- which are related through a complex equilibria and stoichiometry, and hence it results into fractional orders for these species. The reaction can be represented by a pseudo-first-order kinetics where the order in styrene concentration is unity. An apparent activation energy is found as 7.26 kcal/mol.

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