# Epoxidation of styrene to styrene oxide using carbon dioxide and hydrogen peroxide in ionic liquids

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## Abstract

The epoxidation of styrene using hydrogen peroxide and compressed $CO_2$ was conducted in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][$BF_4$]), 1-butyl-3-methylimidazolium hexafluoroborate ([bmim][$PF_6$]), 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1,1,3,3-tetramethylguanidinium lactate [TMG][Lac], 1,1,3,3-tetramethylguanidinium trifluoroacetate [TMG][$CF_3COO$], ethanol, and acetonitrile. It was demonstrated that the reaction could be carried out effectively in [bmim][$BF_4$] or [bmim]Cl without any metallic catalysts. $HCO_4^-$ produced from $CO_2$ and $H_2O_2$ acted as the catalyst. The conversion of styrene and the yield of styrene oxide could reach 95% and 69%, respectively.
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*Keywords:* Epoxidation; Styrene; Hydrogen peroxide; Compressed carbon dioxide; Ionic liquids

## 1. Introduction

Styrene oxide is an important fine chemical intermediate in the production of epoxy resins, cosmetics, surface coatings, sweeteners, perfume, drugs, etc. Styrene oxide can be synthesized by using stoichiometric amount of peracids such as peracetic and *m*-chlorbenzoic acid [1]. However, the employment of peracids leads to equivalent amount of acid waste, which gives rise to environmental pollution. Thus, environmentally friendly methods for epoxidation of styrene with clean oxidant have been a subject of current research. Beside oxygen, much attention has been paid to the use of hydrogen peroxide as a green oxidant because it is cheap and gives water as the only byproduct [2,3]. However, oxidation with hydrogen peroxide is slow in the absence of activation due to the poor leaving tendency of the hydroxide ion [4,5]. A method for activating hydrogen peroxide using bicarbonate ion has been described [6,7]. In this bicarbonate-activated peroxide system, the active species peroxymonocarbonate ion, $HCO_4^-$, is formed from hydrogen peroxide and sodium bicarbonate [6,7]. It is well known that $CO_2$ reacts with water to form carbonic acid. By analogy, the peroxymonocarbonate acid could be formed *via* the reaction of

$CO_2$ and hydrogen peroxide. It was reported that epoxides could be indeed formed in the $CO_2$–$H_2O_2$–$H_2O$ biphasic system using an appropriate base (NaOH) at the appropriate concentration [8–10]. However, the maximum yield of styrene oxide was only 25% in this peroxymonocarbonate system at a $CO_2$ pressure of 241 bar even though organic co-solvents were used.

In recent years, replacing organic solvents with more environmentally benign solvents has attracted much attention. Many ionic liquids (ILs) have gained recognition as environmentally benign solvents due to their unique physical properties such as non-volatility, non-flammability, and thermal stability [11–14]. They have been employed as solvents for a range of chemical processes [15–17]. Numerous catalytic reactions, including biocatalytic reactions, can be carried out in ILs [11,18–21]. Epoxidation reactions in ILs have also been explored [22–24]. Very recently, Chan and co-workers [25] reported that alkenes could be epoxidized using peroxymonocarbonate ion ($HCO_4^-$) generated from the mixture of $H_2O_2$, $CO_2$, NaOH, and water in [bmim][$BF_4$] in the presence of catalytic amount of manganese salt. They conducted the reaction using $CO_2$ at ambient pressure and manganese salt was used in this system because the yields of epoxides were very low in the absence of manganese salt. To the best of our knowledge, there is no report concerning epoxidation of styrene using peroxymonocarbonate ion formed from the reaction between $CO_2$ and hydrogen peroxide without metallic catalysts in ILs.

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Herein, we report our preliminary results on the epoxidation of styrene using hydrogen peroxide and $CO_2$ in ILs. In this route, we coupled the use of hydrogen peroxide, different ILs, KOH, and compressed $CO_2$, and 95% conversion of styrene and 69% yield of styrene oxide were obtained at the appropriate conditions without any metallic catalysts.

## 2. Experimental

### 2.1. Materials

$CO_2$ was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Methylimidazole (99%) were purchased from Acros Organics. 1,1,3,3-Tetramethylguanidine was purchased from BAIQI Chemical Engineering Company and was distilled before use. 1-Chlorobutane, styrene, ethyl acetate, acetonitrile, anhydrous ethanol, trifluoroacetatic acid, lactic acid, and potassium hydroxide were A. R. grade and were purchased from Beijing Chemical Company. Hydrogen peroxide aqueous solution of 30 wt.% was also provided by Beijing Chemical Company.

1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]), 1-butyl-3-methylimidazolium hexafluoroborate ([bmim][PF$_6$]), and 1-butyl-3-methylimidazolium chloride ([bmim]Cl) were prepared using the methods reported literature [26]. The ILs 1,1,3,3-tetramethylguanidinium lactate [TMG][Lac] and 1,1,3,3-tetramethylguanidinium trifluoroacetate [TMG][CF$_3$COO] were prepared by neutralization of 1,1,3,3-tetramethylguanidine and the corresponding acids [27].

### 2.2. Apparatus and procedures

The apparatus for the reaction consisted mainly of a $CO_2$ cylinder, a high-pressure stainless steel reactor with a Teflon coating, a water bath, a pressure gauge, a cold trap, and a magnetic stirrer. The volume of the reactor was 12.4 mL.

As an example, the procedures for the epoxidation of styrene using hydrogen peroxide in [bmim][BF$_4$] are described. In the experiments, 10 mmol [bmim][BF$_4$], 5 mmol styrene, 20 mmol hydrogen peroxide, 1 mmol KOH were loaded into the reactor. The reactor was sealed and placed into the water bath of 40.0 °C, then $CO_2$ was charged into the reactor until a desired pressure was reached, and the system was stirred for 4 h. The reaction was stopped by placing the reactor into ice water and $CO_2$ was released slowly passing through a cold trap containing ethyl acetate to absorb the trace amount of reactant and products entrained by $CO_2$. Then, the reaction mixture in the reactor was extracted with ethyl acetate (4× 10 mL). The organic layer was then washed with saturated brine (15 mL). The extraction mixture was mixed with the ethyl acetate in the trap and was analyzed by GC (Angilent 4890D) with FID detector. The yield of styrene oxide was determined by GC using *N,N*-dimethylformamide as an internal standard. The formation of different products was confirmed by GC–MS (QP 2010). The procedures to conduct the reaction in other solvents were nearly the same. The main difference was that the solvents used were different.

## 3. Results and discussion

In the reaction, styrene oxide was formed along with benzaldehyde, phenylacetaldehyde. The effect of reaction conditions on the epoxidation of styrene was investigated in this work. The total conversion of styrene and the yield of styrene oxide depended strongly on the experimental conditions.

### 3.1. Effect of $CO_2$ pressure

Fig. 1 demonstrates the influence of $CO_2$ pressure on the conversion of styrene and the yield of styrene oxide for the reaction in [bmim][BF$_4$]. The yield is given by moles of styrene oxide produced against the initial moles of styrene used. The reaction did not occurred in the absence of $CO_2$ because there was no active species ($HCO_4{}^-$) required for promoting the reaction in the system. The conversion and the styrene oxide yield increased with increasing $CO_2$ pressure up to 2 MPa, and then remained nearly constant with increase in pressure until 6 MPa. The conversion and the yield decreased with increasing pressure from 6 to 8 MPa, and were nearly constant with further increase of $CO_2$ pressure. This can be explained qualitatively below.

We examined the phase change with the increase of $CO_2$ pressure. There were three phases in the reaction system under low $CO_2$ pressure, the ILs–$H_2O_2$–$H_2O$–styrene phase, the styrene-rich phase and the $CO_2$-rich phase, and the reaction took place in the ILs–$H_2O_2$–$H_2O$–styrene phase. When $CO_2$ pressure increased to 8.0 MPa, the styrene-rich phase and the $CO_2$-rich phase changed into one phase. That is, there were two phases in the system, ILs–$H_2O_2$–$H_2O$–styrene phase and $CO_2$-rich phase. In our system, the pressure of $CO_2$ affects the reaction in two opposite ways. First, the amount of $HCO_4{}^-$ in the system increases with increasing pressure of $CO_2$, which is favorable to enhancing the reaction. Second, the solvent power of $CO_2$ to extract the reactant increases with increasing $CO_2$ pressure. In other words, the amount of the reactant in $CO_2$-rich becomes larger as pressure rises, which reduces the reaction rate because the reaction takes place in the bottom
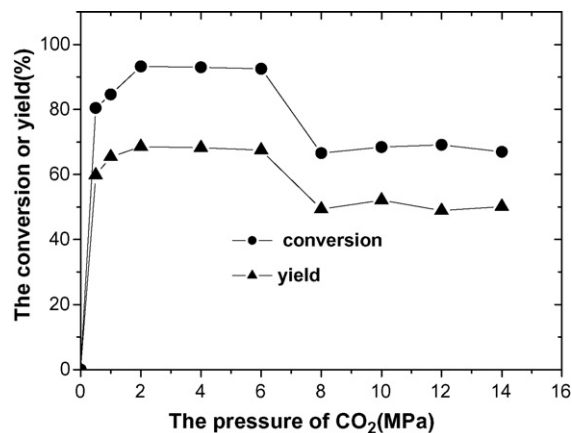


Fig. 1. Effect of $CO_2$ pressure on the styrene conversion and the styrene oxide yield. 10 mmol [bmim][BF$_4$], 5 mmol styrene, 20 mmol $H_2O_2$, 1 mmol KOH, reaction temperature 40.0 °C, reaction time 4 h.

(ILs–$H_2O_2$–$H_2O$–styrene) phase and the styrene molecules in the $CO_2$-rich cannot be converted until they diffuses into the liquid phase. The interface mass transition decreases the reaction rate. The solvent power of $CO_2$ to extract styrene is very poor in the pressure range of 0–2 MPa and most styrene exists in the liquid phase. Therefore the first factor is dominant and the conversion increases with pressure. The two factors compensate each other in the range of 2–6 MPa, and the conversion is nearly independent of pressure. In the pressure range of 6–8 MPa, the solvent power of $CO_2$ increases significantly with increasing pressure because the pressure is near the critical pressure of $CO_2$ [28]. Therefore, the amount of styrene in $CO_2$-rich phase increases more rapidly as pressure increases. In this pressure range the second factor becomes dominant and increase in pressure results in decrease in conversion. At 8 MPa, the solvent power of $CO_2$ is strong enough to extract most styrene, and thus the effect of pressure on the reaction rate is not considerable at higher pressures because most styrene exists in $CO_2$-rich phase.

### 3.2. Effect of KOH

pH of the system has a strong effect on the rate of epoxidation using peroxymonocarbonate ion, and basic condition was favorable to the reaction [7]. In the present work the effect of KOH concentration on the yield of styrene oxide was studied. Fig. 2 shows the dependence of styrene conversion and the yield of styrene oxide on the amount of KOH at 40.0 °C and 2 MPa. The conversion was not noticeable in the absence of KOH because there was little active species ($HCO_4^-$) as shown in reaction (1). The conversion and the yield increased sharply with increasing amount of KOH, and conversion of 95% and yield of 69% could be reached at 0.2 equiv. of KOH, and then the conversion and the yield kept nearly constant with further increase in the amount of KOH. KOH can promote the conversion because it improves the formation of the $HCO_4^-$ ion, which can be known from reactions (2)–(4). It is known that $CO_2$ and KOH can form $HCO_3^-$. In order to provide evidence
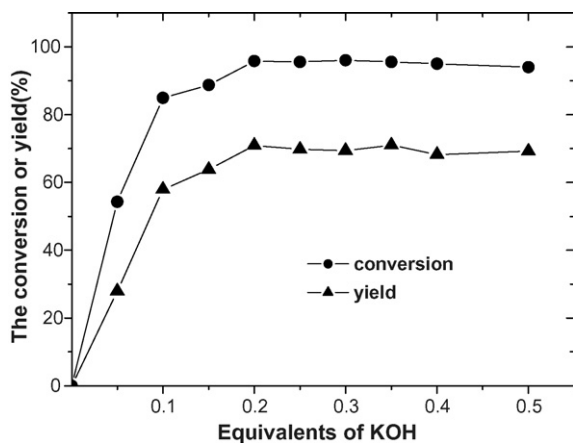


Fig. 2. Effect of equivalents of KOH upon the styrene conversion and the styrene oxide yield. 10 mmol [bmim][BF$_4$], 5 mmol styrene, 20 mmol $H_2O_2$, $CO_2$ pressure 2 MPa, reaction temperature 40.0 °C, reaction time 4 h.
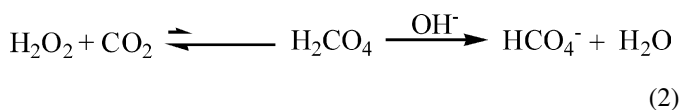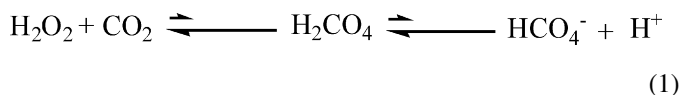
Table 1
Effect of equivalent of $H_2O_2$ on styrene conversion and the styrene oxide yield

| Entry | 30% $H_2O_2$ (equiv.) | Conversion (%) | Yield (%)[a] |
|---|---|---|---|
| 1 | 1 | 45 | 28 |
| 2 | 2 | 79 | 61 |
| 3 | 3 | 89 | 66 |
| 4 | 4 | 95 | 69 |

[a] *Conditions*: 10 mmol [bmim][BF$_4$], 5 mmol styrene, 1 mmol KOH, $CO_2$ pressure, 2 MPa; reaction temperature, 40.0 °C; reaction time, 4 h.

for the argument that $HCO_4^-$ promoted the reaction instead of $HCO_3^-$, we used $NaHCO_3$ to replace $CO_2$ and KOH, and the result demonstrated that no styrene oxide was produced.

$$H_2O_2 + CO_2 \rightleftharpoons H_2CO_4 \rightleftharpoons HCO_4^- + H^+ \tag{1}$$

$$H_2O_2 + CO_2 \rightleftharpoons H_2CO_4 \xrightarrow{OH^-} HCO_4^- + H_2O \tag{2}$$

$$H_2O_2 + OH^- \rightarrow HO_2^- \xrightarrow{CO_2} HCO_4^- \tag{3}$$

$$OH^- + CO_2 \rightarrow HCO_3^- \xrightarrow{H_2O_2} HCO_4^- \tag{4}$$

### 3.3. Effect of equivalent of $H_2O_2$

The conversion of styrene and the yield of styrene oxide depended strongly upon the equivalents of hydrogen peroxide, as can be known from the data in Table 1. The conversion and yield were 45% and 28%, respectively, when the amount of $H_2O_2$ was 1 equiv. The conversion and the yield increased with the increasing of the amount of $H_2O_2$, and as 4 equiv. of $H_2O_2$ was used, 95% styrene conversion and 69% epoxidation yield were achieved along with 12% benzaldehyde and 9% phenylacetaldehyde.

### 3.4. Effect of reaction time

The styrene conversion and the product yield with various reaction times are presented in Table 2. In a relatively short reaction time conversion of styrene was incomplete and the product yield was low. The styrene conversion and product yield increased with reaction time in the range of 0–4 h. However, when the reaction time was prolonged from 4 to 5 h, the styrene oxide yield decreased from 69% to 60% although the styrene

Table 2
Effect of reaction time on styrene conversion and styrene oxide yield

| Entry | Reaction time (h) | Conversion (%) | Yield (%)[a] |
|---|---|---|---|
| 1 | 1 | 40 | 23 |
| 2 | 2 | 72 | 44 |
| 3 | 3 | 90 | 62 |
| 4 | 4 | 95 | 69 |
| 5 | 5 | 98 | 60 |

[a] *Conditions*: 10 mmol [bmim][BF$_4$], 5 mmol styrene, 20 mmol $H_2O_2$, 1 mmol KOH, $CO_2$ pressure 2 MPa, reaction temperature 40.0 °C.

Table 3
Effect of different solvents on the styrene conversion and the styrene oxide yield

| Entry | Solvent (10 mmol) | Conversion (%) | Yield (%)[a] |
|---|---|---|---|
| 1 | [bmim][BF$_4$] | 95 | 69 |
| 2 | [bmim][PF$_6$] | 2 | 0.7 |
| 3 | [bmim]Cl | 65 | 34 |
| 4 | [TMG][CF$_3$COO] | 1 | 0.3 |
| 5 | [TMG][Lac] | 6 | 2 |
| 6 | CH$_3$CH$_2$OH | 3.5 | 1 |
| 7 | CH$_3$CN | 11 | 0.5 |

[a] *Conditions*: 5 mmol styrene, 20 mmol H$_2$O$_2$, 1 mmol KOH, CO$_2$ pressure 2 MPa, reaction temperature 40.0 °C, reaction time 4 h.

conversion increased from 95% to 98%. The reason was that longer reaction time resulted that more styrene oxide was decomposed to benzaldehyde and phenylacetaldehyde. Therefore, the reaction time of 4 h was suitable for this system.

### 3.5. Effect of solvents

Table 3 shows the results of the synthesis of styrene oxide from styrene in different ILs and organic solvents. The data in Table 3 indicate that types of ILs used had significant effect on both styrene conversion and styrene oxide yield. For the imidazolium-based ILs (entries 1–3), the conversion and the yield were very low in [bmim][PF$_6$] because of the poor solubility of H$_2$O$_2$ in [bmim][PF$_6$], which was observed in our experiments. The conversion and the yield in [bmim][BF$_4$] were very high, and those in [bmim]Cl were also satisfactory. We observed that [bmim][BF$_4$] and [bmim]Cl were miscible with H$_2$O$_2$ aqueous solution at our experimental conditions. Therefore, enough HCO$_4^-$ was produced in the IL phase in the presence of CO$_2$, H$_2$O$_2$ and KOH. Table 3 also illustrated that the tetramethylguanidine-based ILs were unfortunately ineffective to the reaction (entries 4 and 5), although they were miscible with H$_2$O$_2$ aqueous solution at our experimental conditions. We can also see from Table 3 that the yield of styrene oxide in [bmim][BF$_4$] and [bmim]Cl were much higher than those in ethanol and acetonitrile. We can conclude that the properties of the solvents affect the reaction significantly. The results also suggest that the imidazolium-based ILs and HCO$_4^-$ have synergetic effect for promoting the reaction. The mechanism for this interesting phenomenon is not clear at this stage.

## 4. Conclusion

The epoxidation of styrene using hydrogen peroxide can be conducted effectively in [bmim][BF$_4$] or [bmim]Cl in the presence of CO$_2$ and KOH without any metallic catalysts. The

properties of the solvents affect the conversion and yield of the reaction significantly. HCO$_4^-$ plays a crucial role in promoting the epoxidation. The imidazolium-based ILs and HCO$_4^-$ show synergetic effect to promote the reaction.

## References

[1] D. Swern (Ed.), Organic Peroxides, vol. 2, Wiley–Interscience, New York, 1971.
[2] G. Grigoropoulou, J.H. Clark, J.A. Elings, Green Chem. 5 (2003) 1.
[3] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
[4] G. Strukul, Catalytic Oxidation with Hydrogen Peroxide as Oxidant, Kluwer, Dordrecht, 1992.
[5] J. Młochowski, S.B. Said, Pol. J. Chem. 71 (1997) 149.
[6] D.E. Richardson, H.R. Yao, K.M. Frank, D.A. Bennett, J. Am. Chem. Soc. 122 (2000) (1729).
[7] H.R. Yao, D.E. Richardson, J. Am. Chem. Soc. 122 (2000) 3220.
[8] S.A. Nolen, J. Lu, J.S. Brown, P. Pollet, B.C. Eason, K.N. Griffith, R. Glaser, D. Bush, D.R. Lamb, C.L. Liotta, C.A. Eckert, G.F. Thiele, K.A. Bartels, Ind. Eng. Chem. Res. 41 (2002) 316.
[9] D. Hancu, J. Green, E.J. Beckman, Acc. Chem. Res. 35 (2002) 757.
[10] D. Hancu, J. Green, E.J. Beckman, Ind. Eng. Chem. 41 (2002) 4466.
[11] R. Sheldon, Chem. Commun. (2001) 2399.
[12] P. Wasserscheid, W. Keim, Angew Chem. Int. Ed. 39 (2000) 3772.
[13] T. Welton, Chem. Rev. 99 (1999) 2071.
[14] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Weirzbicki, J.H. Davis, R.D. Roger, Chem. Commun. (2001) 135.
[15] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids: Industrial Applications to Green Chemistry, ACS Symposium Series 818, American Chemical Society, Washington, DC, 2002.
[16] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley–VCH, Weinheim, 2003.
[17] E.F. Smith, F.J.M. Rutten, I.J. Villar-Garcia, D. Briggs, P. Licence, Langmuir 22 (2006) 9386.
[18] R.A. Sheldon, R.M. Lau, M.J. Sorgedrager, F. van Rantwijk, K.R. Seddon, Green Chem. 4 (2002) 147.
[19] O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo, S. Maietti, Green Chem. 4 (2002) 94.
[20] R.M. Lau, F. van Rantwijk, K.R. Seddon, R.A. Sheldon, Org. Lett. 2 (2000) 4189.
[21] P.B. Webb, M.F. Sellin, T.E. Kunene, S. Williamson, A.M.Z. Slawin, D.J. Cole-Hamilton, J. Am. Chem. Soc 125 (2003) 15577.
[22] C.E. Song, E.J. Roh, Chem. Commun. (2000) 837.
[23] K.H. Tong, K.-Y. Wong, T.H. Chan, Org. Lett. 5 (2003) 3423.
[24] J. Muzart, Adv. Synth. Catal. 348 (2006) 275.
[25] K.-P. Ho, K.-Y. Wong, T.H. Chan, Tetrahedron 62 (2006) 6650.
[26] J. Dupont, C.S. Consorti, P.A.Z. Suarez, R.F. de Souza, Org. Synth. Colloids 10 (2004) 184.
[27] H.X. Gao, B.X. Han, J.C. Li, T. Jiang, Z.M. Liu, W.Z. Wu, Y.H. Chang, J.L. Zhang, Synth. Commun. 34 (2004) 3083.
[28] P.G. Jessop, W. Leitner, Chemical Synthesis using Supercritical Fluids, VCH/Wiley, Weinheim, 1999.