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One-pot synthesis of styrene carbonate from styrene in tetrabutylammonium bromide

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Abstract

Styrene carbonate is synthesized by a direct benign route in the presence of tetrabutylammonium bromide (TBAB) from styrene, compressed CO_2 and *tert*-butyl hydroperoxide (TBHP) as oxidant, in which two sequential reactions of epoxidation and cycloaddition are coupled for a one-pot synthesis. Various reaction parameters, such as CO_2 pressure, reaction temperature and time, TBAB concentration, molar ratio of TBHP to styrene and oxidant types, were investigated. CO_2 pressure was found to play a crucial role in achieving the high yield of styrene carbonate. A plausible reaction mechanism was also proposed.

Keywords: Styrene carbonate; One-pot synthesis; Styrene; Carbon dioxide; Tetrabutylammonium bromide; *tert*-Butyl hydroperoxide

1. Introduction

Cyclic carbonates have gained increasing market demand because of their extensive use as monomers for polycarbonate production, aprotic polar solvents, pharmaceutical/fine chemical intermediates and fuel additives [1,2]. Recently, conventional synthesis using phosgene as a starting material has been replaced by innovative technologies based on cycloaddition of carbon dioxide to epoxides, from the viewpoint of Green Chemistry [3,4] and chemical fixation of CO_2 [5–7]. Epoxides are important intermediates for the manufacture of a range of important commercial products [8]. In the production of cyclic carbonate in current industry, the epoxides are used as substrates, which mainly come from the epoxidation of alkenens [9].

In order to achieve an even more efficient, economic and environmentally friendly process for production of cyclic carbonate, we planned to develop a sequential procedure enabling the synthesis of cyclic carbonate without isolation of intermediate epoxide. The direct oxidative carboxylation of olefins utilizing CO_2 as a building block seems to be a more interesting method, which couples two processes, epoxidation of olefins and CO_2 cycloaddition to epoxides (Scheme 1). It is of practical importance that easily available, low-priced chemicals of olefins are used to produce valuable chemicals. Despite its usefulness, this method has not well been studied so far. Only a few reports are found on the direct synthesis of carbonates using homogeneous catalysts and heterogeneous metal oxide catalysts [6,7,10], which, however, suffer from short lifetime and low yield of the desired carbonates. In addition, up to now other oxidant except O_2 has not been studied in the direct synthesis of carbonate from olefin.

The effective, direct and environmentally benign synthesis of cyclic carbonate with high yield has been the aim of chemists. In our previous work [11], we have found that this task could be efficiently achieved by using tetrabutylammonium bromide (TBAB) as catalyst and solvent. Moreover, the use of any organic solvent was not needed throughout the whole process; in fact, organic solvent removal is of importance to minimize economic cost and environmental impact of chemical processes.

The use of quaternary ammonium salt as catalyst has been extensively studied in organic chemistry. Simple quaternary ammonium salts [12] and onium salts on polymer supports [13] were found to be effective catalysts for the CO_2/epoxide coupling processes to cyclic carbonates. Moreover, quaternary ammonium hydroxide/halide as cocatalyst together with heavy metal salt/compound was used for the direct production of cyclic carbonate from olefins, CO_2 and O_2 [14].

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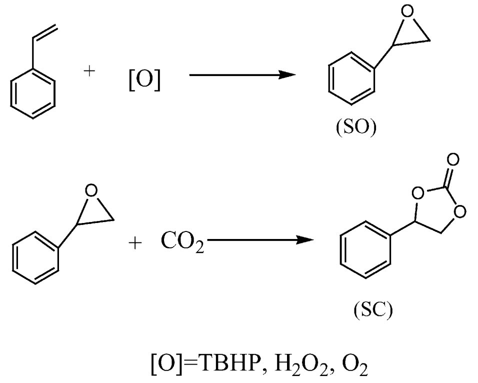


Scheme 1. Two reactions involved in one-pot synthesis of styrene carbonate from styrene and CO_2.

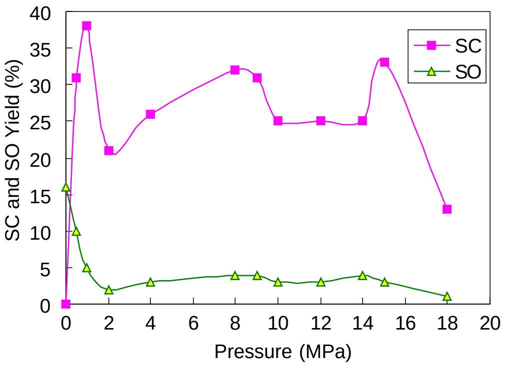


Fig. 1. Effect of CO_2 pressure upon the yields of SC and SO. Styrene, 17.3 mmol; TBHP, 25.4 mmol; TBAB, 2 mmol; 80 °C; 6 h.

On the basis of those previous studies, the present work has been undertaken to apply TBAB for a direct synthesis of styrene carbonate (SC) from styrene and CO_2. As far as we know, no one has so far studied the direct synthesis of styrene carbonate with TBAB as catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant. Effects of reaction parameters, such as CO_2 pressure, temperature, reaction time, TBAB concentration, molar ratio of TBHP to styrene and oxidant types, have been investigated in detail in order to get high yields of styrene carbonate under optimal conditions. And a plausible mechanism in TBAB has also been proposed in this paper.

2. Experimental

Commercial chemicals purchased from Wako, styrene, *tert*-butyl hydroperoxide (70 wt.% in water), hydrogen peroxide (30%), tetrabutylammonium bromide and ethyl acetate, were used as received.

In a typical reaction procedure, TBAB (2 mmol) was added to the mixture of styrene (17.3 mmol) and TBHP (25.4 mmol) in a 50 ml stainless steel autoclave, and then CO_2 was injected to the reactor. An HPLC pump attached with a cooler was used for the supply of CO_2 and the pressure was monitored and controlled by a back pressure regulator. The reactor was stirred continuously at the desired temperature. After the completion of reaction, the reactor was cooled to 0 °C by ice water and depressurized, and then products were dissolved in ethyl acetate. The products were analyzed by a gas chromatograph with a flame ionization detector and further identified by GCMS.

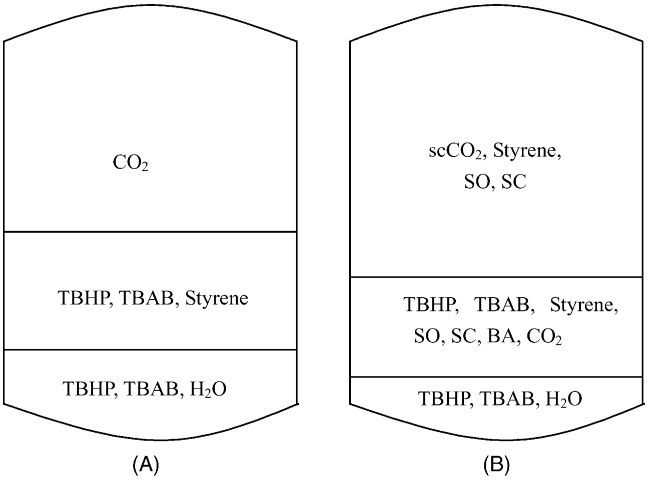
3. Results and discussion

The various reaction parameters in one-pot synthesis of styrene carbonate have been investigated in detail to maximize the yield of SC. Under the various reaction conditions used, SC and styrene epoxide (SO) were formed along with benzaldehyde (BA) and other by-products, which were oligomers of SO and/or SC and some unidentified larger molecules. The total styrene conversion and the product distribution depend strongly on the conditions used, as described in the following. The yield is given by moles of a product formed against the initial moles of styrene used.

3.1. *Effect of CO_2 pressure*

The yields of SC and SO depend strongly upon CO_2 pressure, as illustrated in Fig. 1. The yield of SO decreased sharply in the region up to 2 MPa and then remained nearly constant with further increase in the pressure. The change of SC yield with the CO_2 pressure was complicated. In the absence of CO_2, only epoxidation of styrene occurred, forming SO and BA in yields of 16% and 3%, respectively. When CO_2 was used at 0.5 MPa, the SC and SO yields were 31% and 10%, respectively. This indicates that the addition of CO_2 significantly enhances the epoxidation of styrene and the following carboxylation. As the CO_2 pressure was further raised, the SC yield was maximal at 1 MPa, 8 MPa and 15 MPa. The highest yield of 38% appeared at the lowest pressure of 1 MPa and the slightly lower and comparable yields were observed at higher pressures of 8 MPa and 15 MPa.

The present reaction mixture is a multi-phase system, as illustrated in Scheme 2, and the phase behaviour is of importance in determining the overall reaction rate. The reaction mixture has been visually examined under the reaction conditions with a reactor attached with sapphire windows. Fig. 2 gives the visual observations at different CO_2 pressures. The reaction mixture was in three phases at pressures below 15 MPa, opaque at 15 MPa and transparent at 18 MPa. The overall reaction depends on the volume and properties of the phases, the concentration of reacting species in these phases and the state of contacting among these phases. At lower CO_2 pressures, the volume of the phases hardly changed, but the concentration of CO_2 in the organic phase increased with the pressure. This change may be responsible for the increase of SC yield as observed in Fig. 1. It



Scheme 2. The phases and species present in reaction mixture: (A) before reaction and (B) during reaction.

was previously reported that the epoxidation of olefins was promoted in the presence of CO_2 [15,16] and this may also be significant for the present results. Further introduction of CO_2 caused a dilution of the other reacting species in the organic phase and probably this decreased the SC yield with increasing CO_2 pressure and gave the first maximum around 1 MPa. At higher CO_2 pressures, the volume and properties of the phases changed and several factors should contribute to the reaction in different manners. At present, it is difficult to explain the further change of SC yield observed. Note, however, that the second maximum appeared around 8 MPa near the critical pressure of CO_2. Several previous workers reported similar effects of CO_2 pressure on chemical reactions and a few possible explanations were suggested [17,18]. At 18 MPa, the reaction system was in a single homogeneous phase and so the contacting of reacting species should become better as compared with multi-phase system at lower pressures. At 18 MPa, however, the low concentration of reactants was again responsible for the decrease of SC yield. In addition, oligomers were formed at such high pressures and this was also important. It has been reported that increasing CO_2 pressure is not favourable to the carbonate synthesis through CO_2 addition to propylene oxide [19].

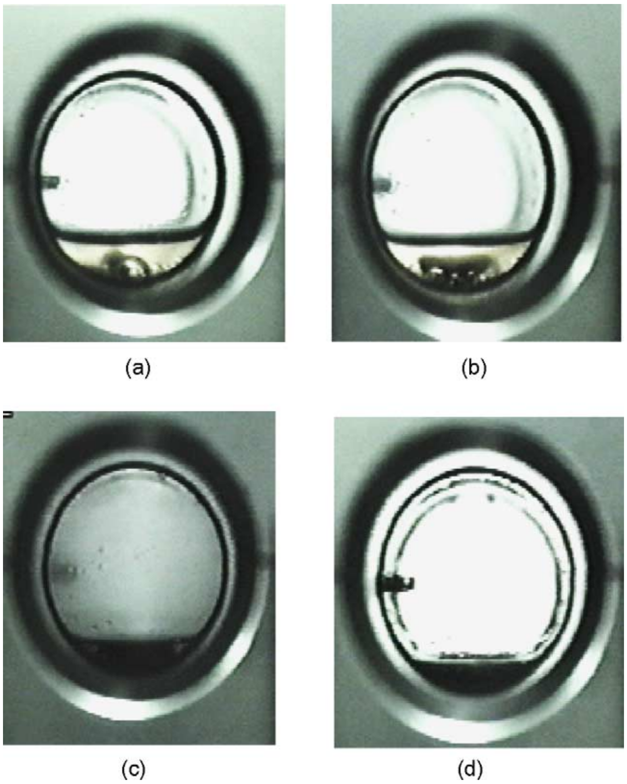


Fig. 2. Photographs of the reactant mixture (styrene, 0.4 ml; TBHP, 0.8 ml; TBAB, 0.4 mmol) taken at CO_2 pressures of (a) 4 MPa, (b) 8 MPa, (c) 15 MPa and (d)18 MPa at 80 °C.

Although it has been reported that the epoxide–CO_2 reaction requires a high pressure of CO_2 [20], in the present direct synthesis of styrene carbonate, the highest yield of carbonate was obtained at the low CO_2 pressure of 1 MPa. The influence of other reaction conditions has been examined at CO_2 pressures of 1 MPa and 15 MPa.

3.2. *Effect of temperature*

The influence of reaction temperature on styrene conversion and product distribution at 1 MPa and 15 MPa was given in Table 1, in which the reaction temperature was varied from 60 °C to 90 °C. At both pressures, the temperature exhibited the same trends. As expected, the styrene conversion increased with the increase in temperature. The SC yield increased with the temperature reaching to the highest at 80 °C. From the visual observations of the reaction mixture, it changed from colorless to yellow at near 78 °C. The color change suggests that TBAB is activated at this temperature, leading to the highest yield of SC at 80 °C. Further increase in reaction temperature (to 90 °C) did not exhibit any significant change in the SC yield. Conversely, the yield of SO increased a little at 90 °C, as the result of the decomposition of SC [21,22]. So, the preferable temperature for the one-pot synthesis of styrene carbonate was 80 °C.

Table 1
Effect of temperature in one-pot synthesis of SC using TBAB

Entry	Temperature (°C)	CO_2 pressure (MPa)	Conversion[a] (%)	Yield[b] (%)		
				SC	SO	BA
1	60	1	55	14	12	2
2	70	1	71	28	10	2
3	80	1	94	38	5	3
4	90	1	97	36	8	3
5	60	15	57	5	5	3
6	70	15	64	15	9	2
7	80	15	74	33	2	5
8	90	15	94	31	5	5

Reaction conditions: TBAB, 2 mmol; styrene, 17.3 mmol; TBHP, 25.4 mmol; time, 6 h.

[a] Total conversion of styrene.

[b] Yield is moles of the product against the initial moles of styrene used.

Table 2
Effect of TBAB concentration in one-pot synthesis of SC using TBAB

Entry	TBAB (mmol)	CO_2 pressure (MPa)	Conversion[a] (%)	Yield[b] (%)		
				SC	SO	BA
1	0	15	50	0	3	3
2	1	1	90	28	7	3
3	2	1	94	38	5	3
4	3	1	95	31	9	2
5	6	1	97	28	16	4
6	1	15	70	17	2	4
7	2	15	74	33	2	5
8	3	15	84	22	4	3
9	6	15	86	19	14	4

Reaction conditions: styrene, 17.3 mmol; TBHP, 25.4 mmol; temperature, 80 °C; time, 6 h.

[a] Total conversion of styrene.

[b] Yield is moles of the product against the initial moles of styrene used.

3.3. *Effect of TBAB concentration*

Table 2 shows the effect of TBAB concentration on the formation of SC. Styrene carbonate was not produced in the absence of TBAB. The amount of SC formed increased with increasing TBAB concentration up to 2 mmol. The SC yield reached maxima of 38% (1 MPa) and 33% (15 MPa) at 2 mmol of TBAB. When TBAB amount was increased above 2 mmol, however, SC yield decreased again and SO yield increased. At 1 MPa, for example, as TBAB amount was increased from 2 mmol to 6 mmol again, the yield of SC decreased from 38% to 28%, while SO yield increased from 5% to 16%. Similar results were also observed at a higher pressure of 15 MPa. Hence, the addition of a larger amount of catalyst TBAB to the reaction mixture has a negative effect on the cycloaddition of CO_2 to SO. Therefore, the optimum TBAB amount was 2 mmol.

3.4. *Effect of molar ratio of TBHP to styrene*

The influence of molar ratio TBHP/styrene in oxidative carboxylation of styrene is listed in Table 3. At both 1 MPa and 15 MPa, the SC selectivities were maximal at a molar ratio of 1.5 (TBHP/styrene). At a higher TBHP concentration (TBHP/styrene = 2), the styrene conversion increased but the SC yield remained almost unchanged, whereas the SO yield increased a little. These results suggest that epoxidation of styrene proceeded more faster than the cycloaddition of CO_2 to epoxide.

Table 3
Effect of molar ratio of reactants in one-pot synthesis of SC using TBAB

Entry	Molar ratio (TBHP/Sty[c])	CO_2 pressure (MPa)	Conversion[a] (%)	Yield[b] (%)		
				SC	SO	BA
1	1	1	92	23	4	2
2	1.5	1	94	38	5	3
3	2	1	99	39	8	2
4	1	15	50	18	2	2
5	1.5	15	74	33	2	5
6	2	15	88	31	4	4

Reaction conditions: TBAB, 2 mmol; temperature, 80 °C; time, 6 h.

[a] Total conversion of styrene.

[b] Yield is moles of the product against the initial moles of styrene used.

[c] Sty: styrene.

Table 4
Effect of reaction time in one-pot synthesis of SC using TBAB

Entry	Time (h)	CO_2 pressure (MPa)	Conversion[a] (%)	Yield[b] (%)		
				SC	SO	BA
1	3	1	79	25	11	2
2	6	1	94	38	5	3
3	8	1	95	33	7	2
4	14	1	100	34	2	4
5	3	15	70	21	7	2
6	6	15	74	33	2	5
7	8	15	86	27	2	4
8	14	15	96	18	3	11

Reaction conditions: TBAB, 2 mmol; styrene, 17.3 mmol; TBHP, 25.4 mmol; temperature, 80 °C.

[a] Total conversion of styrene.

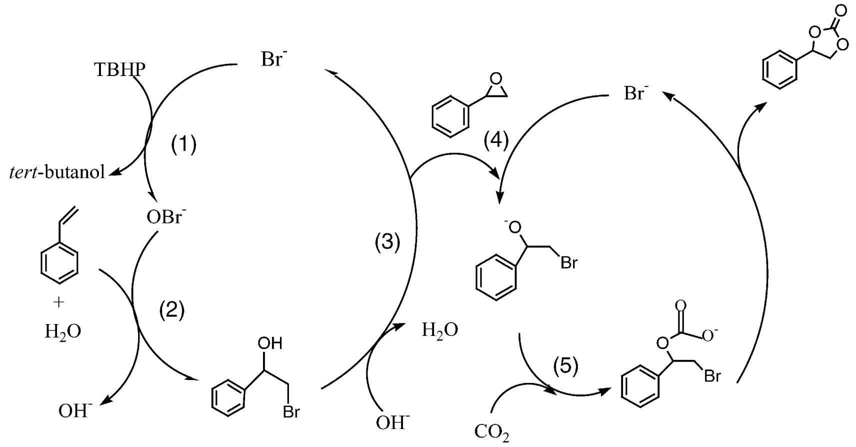
[b] Yield is moles of the product against the initial moles of styrene used.

3.5. *Influence of reaction time*

The conversion and product yields in direct synthesis of SC for various reaction times are presented in Table 4. A relatively short reaction time resulted in incomplete conversion of styrene as well as undesirable product yield. The styrene conversion increased with reaction time in the region of 3–14 h. At 1 MPa, styrene conversion increased markedly from 79% at 3 h to 94% at 6 h, and SC yield was also improved to 38%. When the reaction time was over 6 h, the reaction was almost complete, but SC yield decreased slightly and BA increased a little. However, at a higher pressure of 15 MPa, when the reaction time was increased to 14 h, the yield of SC decreased markedly, but that of BA increased much. Longer reaction time was beneficial for the conversion of styrene, but it was also beneficial to the oxidation of styrene to BA. Therefore, the reaction time of 6 h was suitable for the production of SC.

3.6. *Effect of oxidant*

Table 5 shows the influence of different oxidants, indicating that TBHP is more effective than H_2O_2, although the two reaction systems are alike. When the oxidant was changed to H_2O_2, the yield of SC dropped drastically and much more BA was produced. In addition, only trace amount of SC was obtained along with BA and benzoic acid as main products when O_2 was used as oxidant. The above results suggest that different mechanisms operate when different oxidants are used.



Scheme 3. A proposed mechanism for the direct synthesis of styrene carbonate from styrene and CO_2 in TBAB with TBHP.

3.7. Mechanism considerations

For elucidation of the reaction mechanism, an additional experiment of the first step (styrene epoxidation) was carried out at the same conditions without CO_2. It was observed that the total conversion of styrene was 88% and the yields of SO and BA were 16% and 3%, respectively, indicating that TBAB also catalysed the epoxidation of styrene. Moreover, it has been reported that epoxidation with H_2O_2 can be promoted by bromide over WO_4^{2-} catalysts on layered double hydroxides [23]. Meanwhile, cycloaddition of CO_2 to oxiranes can be catalysed by quaternary onium salts [13,24]. Based on the present and literature results, a reaction mechanism has been postulated, which involves the following steps: (1) catalytic oxidation of Br^- with TBHP leading to the formation of hypobromite OBr^-; (2) bromination of the olefin in the presence of H_2O with the formation of bromohydrin; (3) base-promoted dehydrobromination of the bromohydrin leading to epoxide; (4) ring opening of the epoxide through nucleophilic attack by the bromide ion, producing an oxy anion species; (5) attack by CO_2 forming the cyclic carbonate (Scheme 3).

As mentioned above, there are three phases in the reaction mixture below 15 MPa, which are the aqueous phase, the organic phase and the CO_2-rich gas phase. Step (1) mainly takes place in the organic phase due to higher concentrations of TBHP and TBAB in the organic phase than in the aqueous phase. This difference in the concentrations between the two phases has been suggested from measurements of the concentrations of the reacting species in the different phases under ambient conditions. And steps (2) and (3) should occur significantly at the interfacial layer between the aqueous and organic phases. Steps (4) and (5) should occur in the organic phase dissolving the oxy anion species and CO_2 molecules. The reaction system is so complicated and the reaction result will be influenced by several factors such as intrinsic reactivity of the reacting species, the phase behaviour, the contacting of the phases and the distribution of the reacting species between those phases.

Table 5
Effect of oxidant in one-pot synthesis of SC using TBAB

Entry	Oxidant	Conversion (%)	Yield (%)		
			SC	SO	BA
1[a]	TBHP	74	33	2	5
2[a]	H_2O_2	62	4	2	21
3[b]	O_2	59	1	1	17

[a] Reaction conditions: TBAB, 2 mmol; styrene, 17.3 mmol; TBHP and H_2O_2, 25.4 mmol; temperature, 80 °C; reaction time, 6 h; CO_2 pressure, 15 MPa.

[b] O_2 pressure, 1 MPa; CO_2 pressure, 4 MPa; the other conditions are the same as for a.

4. Conclusions

The direct synthesis of styrene carbonate from styrene and CO_2 is attractive because starting materials are easily available and cheap, preliminary synthesis of styrene epoxide is avoided, and the work-up procedures are simple. With TBHP as oxidant a moderate yield of SC can be obtained in the presence of TBAB, in the absence of additional organic solvents in the whole reaction. The SC yield can reach 38% at optimum reaction conditions. Although the SC yield obtained in the present work is still not satisfactory for practical applications, it is much better compared with the previous works [6,7,10], in which benzaldehyde is the main product and the carbonate yield is very low (only 4%). It should be noted, moreover, that organic solvents and high reaction temperatures are not needed in our reaction systems, which are beneficial from the environmental and energy-saving point of view.

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References

[1] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.

[2] K. Weissermel, H. Arpe (Eds.), Industrial Organic Chemistry, third ed., Wiley-VCH, Weinheim, New York, 1997.

[3] B.M. Trost, Science 254 (1991) 1471.

[4] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998.

[5] S. Fujita, B.M. Bhanage, Y. Ikushima, M. Shirai, K. Torii, M. Arai, Catal. Lett. 79 (2002) 95.

[6] M. Aresta, A. Dibenedetto, J. Mol. Catal. A Chem. 182 (2002) 399.

[7] M. Aresta, A. Dibenedetto, I. Tommasi, Appl. Organomet. Chem. 14 (2000) 799.

[8] K. Bauer, D. Garbe, H. Surburg, Common Fragrance and Flavour Materials, Wiley-VCH, Weinheim, New York, 1997.

[9] G. Scienel, R. Rieth, K.T. Rowbottom, Ullmann's Encyclopedia of Organic Chemicals, Wiley-VCH, Weinheim, New York, 1999.

[10] J.L. Kao, G.A. Wheaton, H. Shalit, M.N. Sheng, US Patent 4247465 (1981).

[11] J.M. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Commun. 5 (2004) 83.

[12] A. Behr, Carbon Dioxide Activation by Metal Complexes, Wiley-VCH, Weinheim, New York, 1998, p. 91.

[13] T. Nishikubo, A. Kameyama, J. Yamashita, M. Tomoi, W. Fukuda, J. Polym. Sci. 31 (1993) 939.

[14] J.A. Verdol, US Patent 3025305 (1962).

[15] T. Danciu, E.J. Beckman, D. Hancu, R.N. Cochran, R. Grey, D.M. Hajnik, J. Jewson, Angew. Chem. Int. End. 42 (2003) 1140.

[16] D.R. Pesiri, D.K. Morita, W. Glaze, W. Tumas, Chem. Commun. (1998) 1015.

[17] M. Arai, Y. Nishiyama, Y. Ikushima, J. Supercrit. Fluids 13 (1998) 149.

[18] P.G. Jessop, W. Leitner (Eds.), Chemical Synthesis Using Supercritical Fluids, Wiley-VCH, Weinheim, New York, 1999 (Chapter 4.3).

[19] B.M. Bhanage, S. Fujita, Y. Ikushima, K. Torii, M. Arai, Green Chem. 5 (2003) 71.

[20] N. Kihara, N. Hara, T. Endo, J. Org. Chem. 58 (1993) 6198.

[21] B.M. Bhanage, S. Fujita, Y. Ikushima, K. Torii, M. Arai, Appl. Catal. A Gen. 219 (2001) 259.

[22] R.M. Weinstein, US Patent 481555 (1989).

[23] B.F. Sels, D.E. De Vos, P.A. Jacobs, J. Am. Chem. Soc. 123 (2001) 8350.

[24] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.