

Cycloaddition of styrene oxide and CO₂ mediated by pyrolysis of urea†Cite this: *RSC Advances*, 2013, 3, 14290Received 7th June 2013,
Accepted 25th June 2013

DOI: 10.1039/c3ra42803f

www.rsc.org/advances

Jose Tharun, Dong Woo Kim, Roshith Roshan, Amal Cherian Kathalikkattil,
Manickam Selvaraj and Dae-Won Park*

This paper reports the effectiveness of carrying out the cycloaddition reaction of styrene oxide (SO) and CO₂ without the use of any catalysts. A naturally abundant and cheap material, urea, was utilized in promoting the reaction by controlling the reaction conditions. The influence of reaction temperature, carbon dioxide (CO₂) pressure, amount of urea, and the reaction time on the selectivity of styrene carbonate (SC) was investigated.

Introduction

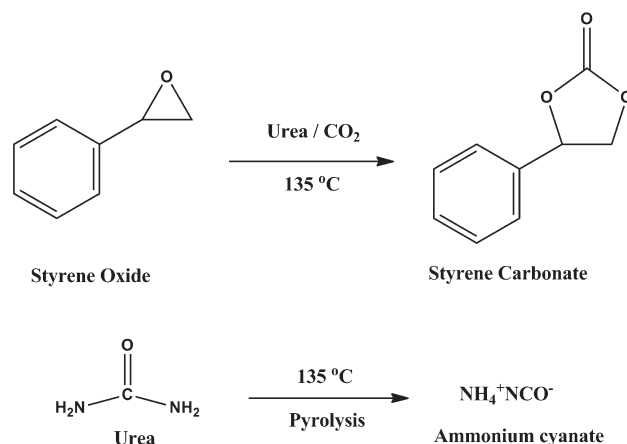
A lot of research has been done on carbon dioxide (CO₂) transformations, where CO₂ is used as a raw material in many reactions, and these methods offer one of the most efficient ways to reduce the atmospheric CO₂ concentrations.¹ Cyclic carbonates are attractive and important compounds in a variety of chemical research fields, which could be obtained by the coupling reaction of CO₂ and epoxides. Because of their high solubilizing power, high boiling and flash points, low odor levels and evaporation rates, low toxicities, and biodegradability; cyclic carbonates are utilized as aprotic polar solvents in degreasing, paint stripping, and cleaning processes. Similar to linear dialkyl carbonates, cyclic carbonates are useful as intermediates for the synthesis of polycarbonates, electrolytes in lithium ion batteries, or green solvents.² A wide variety of catalysts have been employed for the synthesis of cyclic carbonates in which the catalysts possessing strong nucleophilic groups showed better activity,^{1–3} where in anionic group helps in the ring opening of epoxides for an effective CO₂ cycloaddition.^{1,2}

Urea is the major metabolic end product of nitrogen substances in the human body. Being a naturally available, cheap, and abundant material, it would be an excellent choice to utilize urea as a starting material for the synthesis of various important industrial products. In this regard, synthesis of glycerol carbonate from glycerol and urea is one of the promising areas of research.⁴

The synthesis of cyclic carbonates from urea and diols have been reported by Li *et al.*^{5a} and Zhou *et al.*^{5b} using metal oxides and metal carbonates, respectively, as the catalysts. On another aspect, the synthesis of cyclic carbonates from epoxides and CO₂ has been carried out by Han *et al.* using choline chloride/urea as a heterogeneous catalyst system.⁶ In this study, styrene carbonate (SC) has been synthesized from CO₂ and styrene oxide (SO) in the presence of urea at high temperatures under solvent free conditions (Scheme 1). The reactivity of urea could be controlled by varying the reaction conditions for the selective production of SC.

Result and discussion

Due to the inert nature of CO₂, its activation and incorporation into organic substances is a daunting task. We investigated the crucial role of temperature and CO₂ pressure in the synthesis of SC from SO and CO₂ mediated by the pyrolysis of urea. Fig. 1 shows the influence of temperature on the yield and selectivity of SC. It can be seen clearly that the catalytic activity is sensitive to reaction temperature. At 80 °C, no reaction took place; upon raising the

Scheme 1 Cycloaddition of styrene oxide and CO₂.

Division of Chemical and Biomolecular Engineering, Pusan National University,
Busan 609-735, Korea. E-mail: dwpark@pusan.ac.kr; Fax: +82 51 512 8563; Tel: +82
51 510 2399

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra42803f

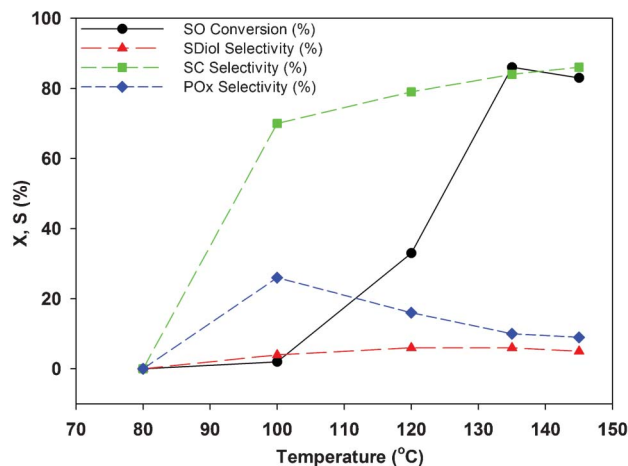


Fig. 1 Effect of reaction temperature. Reaction conditions: SO = 18.6 mmol, urea amount = 0.1 g, P_{CO_2} = 2.0 MPa, time = 12 h.

temperature from 100 °C to 120 °C, there was a slight increase in percentage conversion and reached a maximum conversion of 86% with 84% selectivity of SC at 135 °C, beyond which no further increase in activity was observed. This could be explained on the basis of thermal decomposition of urea (or pyrolysis of urea). Urea is thermally stable up to 133 °C, after which it decomposes to an intermediate called ammonium cyanate. The main requirement for cycloaddition of epoxides and CO_2 is the availability of an anionic species that helps in the ring opening of epoxides.^{1,2} Urea decomposing to ionic ammonium cyanate salt at 135 °C is the main reason for the reactivity in the cycloaddition reaction of SO and CO_2 .⁷ The other byproducts obtained during cycloaddition of SO and CO_2 were 2-oxazolidinone (POx) and styrene diol (SDiol) with 10% and 6% selectivity respectively at the best reaction condition (2.0 MPa, 12 h, 135 °C).

Fig. 2 depicts the effect of CO_2 pressure on the cycloaddition of SO and CO_2 in the presence of urea at 135 °C for 12 h. It can be

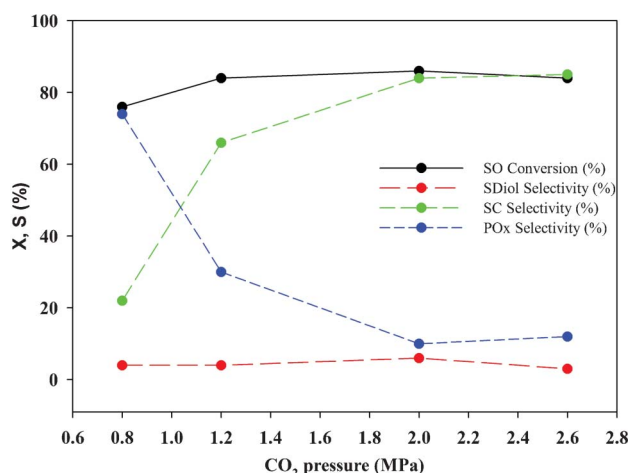


Fig. 2 Effect of CO_2 pressure. Reaction conditions: SO = 18.6 mmol, urea amount = 0.1 g, T = 135 °C, time = 12 h.

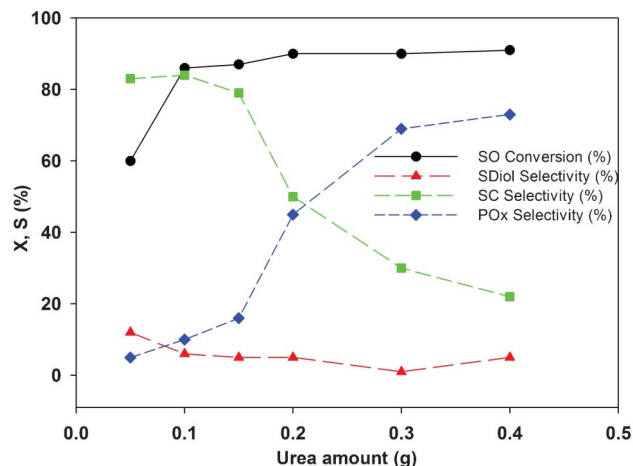


Fig. 3 Effect of urea amount. Reaction conditions: SO = 18.6 mmol, P_{CO_2} = 2.0 MPa, T = 135 °C, time = 12 h.

seen that the initial CO_2 pressure has a great influence on the percentage yield of SC. As more and more CO_2 was applied to the reaction, the conversion of SO increased, with an increase in SC selectivity, while that for POx decreased. The conversion of SO shows a steady increase with the increase in CO_2 pressure from 0.8 MPa to 2.0 MPa, and reaches a maximum of 86% conversion. Further increase in CO_2 pressure beyond 2.0 MPa did not bring in much of a change, while in fact slightly decreased the reactivity. This observation can be explained by the effect of pressure on the concentrations of CO_2 and SO in the two phases (liquid and gas). The upper phase in the reactor is the CO_2 -rich phase (gas), and the bottom phase is the SO-rich phase (liquid). The reactions take place mainly in the liquid phase because the urea is dispersed in this phase. At first, the solubility of gaseous CO_2 in liquid SO increases with increasing pressure, which favors the reaction to proceed. At higher pressures, however, more and more SO becomes dispersed in the gaseous CO_2 -rich phase resulting in a lower concentration in the liquid phase which reduces the rate of reaction.⁸

The influence of urea amount on the reaction was also evaluated and illustrated in Fig. 3. When the amount of urea was doubled (0.05 g to 0.1 g), the percentage conversion of SO also increased from 60% to 86%. Further increase in the amount of urea did not change the percentage conversion of SO significantly.

It can be explained by the fact that an excess of urea cannot be well dispersed in the reaction mixture and so limits the mass transfer between the active sites and the reactants.⁹ As a result, 0.1 g of urea was chosen as the optimal amount of urea in the present cycloaddition reaction process. Moreover, as the amount of urea increased, the selectivity for POx also increased in the reaction. In a similar system, it was witnessed that at first the epoxide undergo cycloaddition with CO_2 , forming a cyclic carbonate, followed by reaction with amino alcohols to produce 2-oxazolidinones.¹⁰

The dependence of the product yield on the reaction time at 135 °C and 2 MPa CO_2 pressure is shown in Fig. 4. The percentage conversion of SO increased with the reaction time and reached a maximum yield of 86% after 12 h. The percentage conversion of

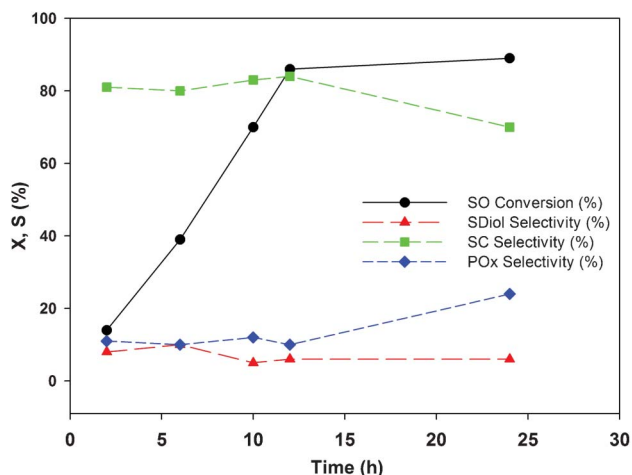
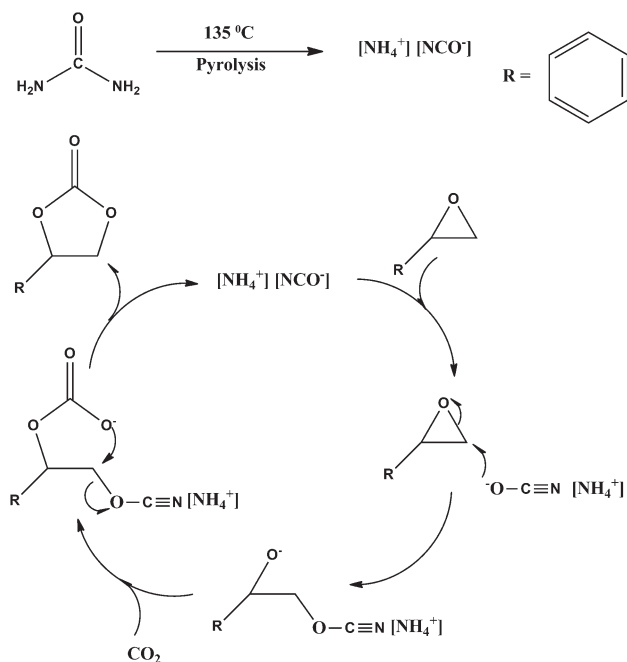


Fig. 4 Effect of reaction time. Reaction conditions: SO = 18.6 mmol, urea amount = 0.1 g P_{CO_2} = 2.0 MPa, T = 135 °C.

SO did not show any improvement by prolonging the reaction time beyond 12 h, indicating that 12 h is the optimal reaction time for the urea pyrolysis mediated cycloaddition reaction of SO and CO_2 . Concomitant with the results, we propose a plausible mechanism in which the intermediate ammonium cyanate obtained by the urea pyrolysis at 135 °C attacks the β carbon atom of the SO (less hindered), followed by cycloaddition of CO_2 , resulting in the formation of cyclic carbonate (Scheme 2).



Scheme 2 Proposed mechanism of urea mediated cycloaddition.

Conclusions

SC has been successfully prepared by the cycloaddition of SO and CO_2 in the presence of urea at 135 °C. Urea pyrolysis occurring at 135 °C results in the formation of ionic ammonium cyanate salt intermediate which helps in the epoxide ring opening of SO followed by cycloaddition of CO_2 to form SC. The influence of CO_2 pressure, reaction temperature, urea amount and reaction time, in selectively yielding SC product has been investigated. This work shows the effectiveness of carrying out cycloaddition reaction of SO with CO_2 exploring the earlier thermal degradation of a naturally abundant cheap material, urea instead of employing a conventional catalyst.

Experimental

Urea ($\geq 99\%$) and styrene oxide (SO) (97%) were purchased from Aldrich and used without further purification. Carbon dioxide of 99.999% purity was used without further purification. Dichloromethane was obtained from SK Chemicals, Korea, and used as received.

The formation of intermediate ammonium cyanate from urea at 135 °C was confirmed by the DSC-TGA (11.47 mg of urea on an SDT Q600 V20.9 Build 20 apparatus under a nitrogen flow of 100 mL min^{-1} using a heating rate of 5 °C min^{-1} from room temperature to 400 °C) kept in supplementary data. The synthesis of SC from SO and CO_2 (Scheme 1) in the presence of urea was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical batch operation, urea (0.05–0.4 g) and SO (18.6 mmol) were charged into the reactor without adding any solvent, and purged by CO_2 several times. The reactor was then pressurized with CO_2 to a preset pressure, at room temperature. The reaction was carried out by heating the reactor to a desired temperature while stirring the reaction mixture at 600 rpm. After a time period, the cycloaddition reaction was stopped by cooling the reaction mixture to room temperature and venting the remaining unreacted CO_2 . Product analysis was carried out by gas chromatography/mass spectrometry (GC-MS, Micromass, UK) analysis. ^1H NMR (Varian 500 MHz, CDCl_3) δ (ppm): 7.36–7.43 (5H), 5.6 (1H), 4.8 (1H), 4.3 (1H). The percentage conversion of SO was measured by gas chromatography (GC, HP 6890, Agilent Technologies, Santa Clara, CA, USA) data.

Acknowledgements

This study was supported by the Korean Ministry of Education through the National Research Foundation (NRF 2012-001507) and the Global Frontier Program.

References

- (a) S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479; (b) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539; (c) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- (a) A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951–976; (b) M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ.*

- Sci.*, 2010, **3**, 43–81; (c) W. L. Dai, S. L. Luo, S. F. Yin and C. T. Au, *Appl. Catal., A*, 2009, **366**, 2–12.
- 3 (a) T. Sakakura, J. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387; (b) J. Tharun, M. M. Dharman, Y. Hwang, R. Roshan, M. S. Park and D. W. Park, *Appl. Catal. A*, 2012, **419–420**, 178–184; (c) J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A. C. Kathalikkattil and D. W. Park, *Catal. Sci. Technol.*, 2012, **2**, 1674–1680; (d) J. Tharun, D. W. Kim, R. Roshan, Y. Hwang and D. W. Park, *Catal. Commun.*, 2013, **31**, 62–65; (e) K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G. A. Park and D. W. Park, *Green Chem.*, 2012, **14**, 2933–2940.
- 4 (a) C. Hammond, J. A. Lopez-Sanchez, M. H. A. Rahim, N. Dimitratos, R. L. Jenkins, A. F. Carley, Q. He, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Dalton Trans.*, 2011, **40**, 3927–3937; (b) M. Aresta, A. Dibenedetto, F. Nocito and C. Ferragina, *J. Catal.*, 2009, **268**, 106–114; (c) M. J. Climent, A. Corma, P. D. Frutos, S. Iborra, M. Noy, A. Velty and P. Concepcion, *J. Catal.*, 2010, **269**, 140–149.
- 5 (a) Q. Li, W. Zhang, N. Zhao, W. Wei and Y. Sun, *Catal. Today*, 2006, **115**, 111–116; (b) J. Zhou, D. Wu, B. Zhang and Y. Guo, *Chem. Ind. Chem. Eng. Q.*, 2011, **17**, 323–331.
- 6 A. Zhu, T. Jiang, B. Han, J. Zhang, Y. Xie and X. Ma, *Green Chem.*, 2007, **9**, 169–172.
- 7 (a) P. M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach and J. Brauer, *Thermochim. Acta*, 2004, **424**, 131–142; (b) V. Ebrahimian, A. Nicolle and C. Habchi, *AIChE J.*, 2012, **58**, 1998–2009; (c) L. Stradella and M. Argentero, *Thermochim. Acta*, 1993, **219**, 315–323.
- 8 (a) J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai and L. N. He, *J. Mol. Catal. A: Chem.*, 2006, **249**, 143–148; (b) Y. Xie, Z. F. Zhang, T. Jiang, J. L. He, B. X. Han, T. B. Wu and K. L. Ding, *Angew. Chem., Int. Ed.*, 2007, **46**, 7255–7258; (c) L. F. Xiao, F. W. Li, J. J. Peng and C. G. Xia, *J. Mol. Catal. A: Chem.*, 2006, **253**, 265–269.
- 9 J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng and S. Zhang, *Catal. Today*, 2009, **148**, 361–367.
- 10 Y. P. Patil, P. J. Tambade, S. R. Jagtap and B. M. Bhanage, *J. Mol. Catal. A: Chem.*, 2008, **289**, 14–21.