Chemical fixation of carbon dioxide to styrene carbonate under supercritical conditions with DMF in the absence of any additional catalysts

Hajime Kawanami*[ab] and Yutaka Ikushima[ab]

[a] National Industrial Research Institute of Tohoku, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan. E-mail: h-kawa@tniri.go.jp
[b] CREST, (JST), Tokyo 102-8666, Japan Science and Technology Corporation, Japan

Chemical fixation of carbon dioxide to styrene carbonate proceeds effectively under supercritical conditions with DMF even in the absence of any additional catalysts, giving a maximum yield of 85% in the near-critical region.

From the standpoint of the protection of environment, the development of an environmentally benign process utilizing carbon dioxide, which is one of the greenhouse-effect gases, has drawn current interest in industrial chemistry and biotechnology. Chemical fixation of carbon dioxide is one of the most attractive methods for the development of a truly environmentally benign process since there are many possibilities for carbon dioxide to be used as a safe and cheap C_1 component to produce useful organic compounds. The conversion of carbon dioxide into carbonates has been carried out in conventional organic solvents using catalysts such as dialkyltin methoxide,[1] organoantimony halide,[2] alkali metal salts[3] and Mg–Al mixed metal oxide.[4] In particular, the conversion of epoxides into five-membered cyclic carbonates is industrially of great importance. However, these reactions using metallic catalysts have disadvantages, such as poor solubility of the catalyst[3] and difficulties in catalyst recycling,[2] whereas $scCO_2$ has advantageous features such as the disappearance of a gas–liquid phase boundary and easily tunable properties with pressure and temperature which make $scCO_2$ an alternative to conventional solvents.[5] The reactions of epoxides with CO_2 under supercritical CO_2 conditions have been studied in the presence of zinc catalysts; however, they give a biphasic mode of operation leading to poor reaction rates.[6] It has recently been found that the reaction with epoxide and CO_2 proceeds in DMF alone without any catalysts at temperatures around 135 °C and atmospheric CO_2 pressure, but the yield of styrene carbonate still remains low.[4,7] This low reactivity may be due to a much lower mass transfer of epoxide in DMF solution, although DMF is considered to catalyze the reaction in a manner similar to the

Mg–Al mixed catalysts.[4] Thus, our conception of using a co-solvent such as DMF both as a catalyst as well as a solvent in $scCO_2$ has emerged to improve the poor reaction rates, which are due to limitations in liquid–liquid mass transfer and/or low solubility of reactants.[5] DMF itself catalyzes the reactions of CO_2 with epoxides dissolved in DMF–$scCO_2$ which allows to advantage a reduction in viscosity and an increase in diffusion rate as compared with the DMF liquid phase.[8] Here we demonstrate integration of $scCO_2$ and DMF to accelerate the reaction of styrene oxide with CO_2 and to be a very powerful tool in the chemical fixation of CO_2 (Scheme 1).†

Carboxylation of styrene oxide with CO_2 has been conducted without additional catalysts under various conditions (see Table 1). Under these conditions, carbonate was the main product with trace amounts of a few by-products.‡ In acetone and acetonitrile, styrene oxide did not react with CO_2 and styrene carbonate was not obtained (runs 2 and 3). It is noteworthy that the conversion proceeds successfully even in the absence of the metallic catalysts used so far when DMF is used in the place of acetone and acetonitrile (run 1). This is believed to be due to catalysis by DMF itself because the substrates, styrene oxide and CO_2, have similarly finite solubilities in acetone and acetonitrile as well as DMF. When $scCO_2$ alone was used as medium instead of DMF, a very poor reaction was obtained (run 7), and the catalytic action of $scCO_2$ for this reaction was found to be negligibly small. In the case of the CO_2–DMF system at lower pressures such as 2.0 MPa (run 1), the yield of styrene
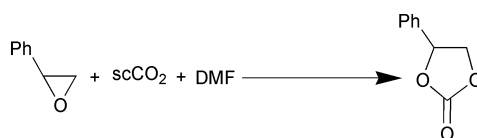
Scheme 1

Table 1 Carboxylation of epoxides with carbon dioxide in different reaction systems

Run	Reaction type	Substrate	Catalyst	Solvent system	Pressure/ MPa	Temperature/°C	Yield of carbonate (%)[a]
1	Biphasic		None	DMF–CO_2	2.0	135	29
2[b]	Biphasic		None	Acetone–CO_2	2.0	135	0
3[b]	Biphasic		None	Acetonitrile–CO_2	2.0	135	0
4	Biphasic		None	DMF–CO_2	2.0	107	0
5	Homogeneous		None	DMF–$scCO_2$	7.9	100	20
6	Homogeneous		None	DMF–$scCO_2$	7.9	150	85
7	Homogeneous		None	$scCO_2$	7.9	120	3.2
8[c]	Biphasic		MgO	DMF–CO_2	2.0	135	60
9	Homogeneous		None	DMF–$scCO_2$	7.9	120	83
10[d]	Biphasic		Mg–Al mixed oxide	DMF–CO_2	0.5	100	90(86)[e]

[a] The yields are determined by GC analysis based on the area ratio of tridecane or tetradecane as the internal references. [b] Reaction conditions: acetonitrile 5 mmol or acetone 5 mmol; styrene oxide 5 mmol; reaction time 15 h. [c] Ref. 7. [d] Ref. 4. [e] K. Yamaguchi *et al.* reported similar yields of the carbonate.
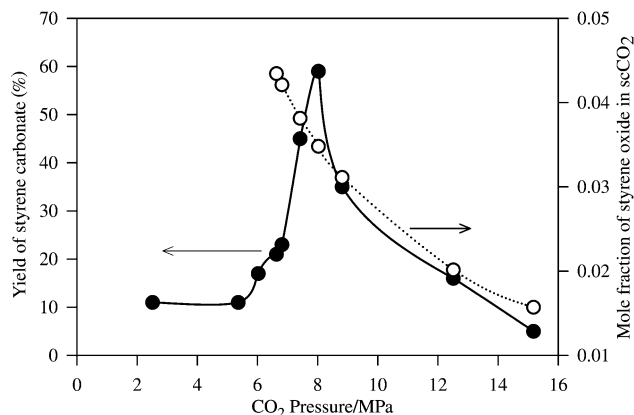
Fig. 1 Pressure dependence of the yield of styrene carbonate in CO_2 in the presence of DMF at 120 °C, and mole fraction of styrene oxide in $scCO_2$. Reaction time is 15 h. Mole fraction of styrene oxide was calculated using PROPATH Ver.10.2.

carbonate remains as low as 29%, whereas $scCO_2$–DMF (run 6) provides a much better yield compared with the CO_2–DMF system (29 to 85%) and the DMF–MgO system (60 to 85%). Furthermore, it was found that in the $scCO_2$–DMF system (run 5) styrene carbonate can be successfully synthesized even at lower temperatures around 100 °C, giving a better yield than that in the CO_2–DMF system (run 4) at 107 °C (0 to 20%). Gas–liquid–liquid mass transfer together with liquid–liquid mass transfer (solubility of substrate in catalyst or solvent phase) are important parameters for controlling the reaction yield. Visual observation through a sapphire window confirms that this $scCO_2$–DMF system forms a homogeneous reaction system, resulting in complete elimination of gas–liquid mass transfer, so that transport to and from the DMF phase is no longer a limiting factor. This is considered to be one of the most effective factors that cause the significant increase in yield as observed in Table 1.§ We have further attempted the conversion into another epoxide, 1,2-epoxy-3-phenoxypropane, using the $scCO_2$–DMF system at 7.9 MPa and 120 °C (run 9). This $scCO_2$–DMF system gives a good conversion to 3-phenoxy-1,2-propylcarbonate, the yield being comparable to that of the DMF–Mg/Al mixed oxide system (run 10). So this system can be available for acceleration of conversion from epoxides to carbonates.

Fig. 1 shows the pressure dependence of the yield of styrene carbonate in CO_2 in the presence of DMF at 120 °C. One can see an interesting pressure dependence in which the yield significantly increases, reaching a maximum yield at 7.9 MPa near the critical pressure of CO_2, and then sharply decreases with increasing pressure. In the lower pressure range below about 7 MPa, the yields are very small; DMF remains insoluble (by visual observation), leading to a much lower transfer of the epoxide. However, approach to the critical pressure with increasing pressure, which can dissolve DMF, significantly increases the rate of reaction and a higher yield is observed. On the other hand, the remarkable decrease in yield observed at higher pressures beyond 7.9 MPa near the critical pressure cannot be fully explained by the thermodynamic pressure effect, in which an increase in pressure is predicted to cause an enhancement in the reaction rate.[9] All experiments in the higher pressure range were confirmed by visual observation to take place in a single phase. To explain the decrease in yield with increasing pressure, we have attempted to introduce the mole fraction of styrene oxide in $scCO_2$ as shown in Fig. 1. It is evident that the extent of the decrease in yield of styrene carbonate is in agreement with that in mole fraction of styrene

oxide except at 7.9 MPa near the critical pressure. If the reaction of styrene oxide with CO_2 is to take place by the catalysis of DMF, the molecules of styrene oxide and DMF must come into contact or very nearly so. Consequently, the decrease in mole fraction of styrene oxide in the higher pressure region prevents contact with DMF and reduces the yield of styrene carbonate. However, in the near-critical region the yield at 7.9 MPa is significantly higher than that expected from the relationship in Fig. 1, which cannot be accounted for only by the change in mole fraction of styrene oxide. It is likely that the increased local concentration[10,11] of the styrene oxide and/or CO_2 around the DMF is influencing the reaction, which becomes more pronounced at lower pressures in the near-critical region.[12,13] Thus, in the present conversion to styrene carbonate, the local concentration of reactants would be very large at 7.9 MPa near the critical pressure, resulting in the significant increase of the yield as seen in Fig. 1.

In conclusion, $scCO_2$–DMF was shown to be a good alternative catalytic system for conventional biphasic catalytic systems. It was further demonstrated that the yield of carbonates can be enhanced just by pressure manipulation of the $scCO_2$–DMF system.

Notes and references

† Typical experimental procedure is as follows: styrene oxide (5 mmol) was dissolved in DMF (5 mmol) in a 50 cm³ reactor at rt, and then the mixture was heated up to the desired temperature and CO_2 (7.9 MPa) was introduced into the reactor. In the case of the $scCO_2$–DMF system, liquid CO_2 was subsequently charged into the reactor using a high-pressure liquid pump and compressed to the desired pressure. Pressure control was achieved by a back-pressure regulator. The reactions in both the CO_2–DMF and $scCO_2$–DMF systems were started by stirring the mixture and continued for 15 h. After the reaction, the pressure was released and the crude product was analyzed by NMR and GC-MS spectroscopy. The yields of carbonates were determined by GC-MS using tridecane or tetradecane as an internal standard.

‡ The total amount of these minor products is less than 1% from the GC analyses.

§ Another factor is thought to be solvation effect of CO_2, and studies on the solvation effect by IR and NMR are now in progress.

1 There are too many reports to list here. One of the latest reports dealing with carbonate is: J.-C. Choi, T. Sakakura and T. Sako, *J. Am. Chem. Soc.*, 1999, **121**, 3793.
2 H. Matsuda, A. Ninagawa, R. Nomura and T. Tuschida, *Chem. Lett.*, 1979, 573.
3 N. Kihara, N. Hara and T. Endo, *J. Org. Chem.*, 1993, **58**, 6198.
4 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.
5 P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 687; Y. Ikushima and M. Arai, *Chemical Synthesis using Supercritical Fluids*, P. G. Jessop and W. Leitner, eds., Wiley-VCH, Weinheim, 1999, ch. 4.3.
6 D. J. Darensbourg, N. W. Stafford and T. Katsurao, *J. Mol. Catal. A: Chem.*, 1995, **104**, L1.
7 T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1997, 1129.
8 B. M. Bhanage, Y. Ikushima, M. Shirai and M. Arai, *Tetrahedron Lett.*, 1999, **40**, 6427; B. M. Bhanage, Y. Ikushima, M. Shirai and M. Arai, *Chem. Commun.*, 1999, 1277.
9 J. B. Ellington and J. F. Brennecke, *J. Chem. Soc., Chem. Commun.*, 1993, 1094.
10 Y. Ikushima, N. Saito, M. Arai and H. W. Blanch, *J. Phys. Chem.*, 1995, **99**, 8941.
11 T. W. Randolph, D. S. Clark, H. W. Blanch and J. M. Prausnitz, *Science*, 1988, **239**, 387.
12 S. Kim and K. P. Johnston, *AIChE J.*, 1987, **33**, 1603.
13 R. Wu, L. L. Lee and H. D. Cochran, *Ind. Eng. Chem. Res.*, 1990, **29**, 977.