

Effective scCO₂-ionic Liquid Reaction System Based on Symmetric Aliphatic Ammonium Salts for the Rapid CO₂ Fixation with Aziridine to 2-Oxazolidinone

Hajime Kawanami,* Hajime Matsumoto,[†] and Yutaka Ikushima

Supercritical Fluid Research Center, National Institute of Advanced Science and Technology, and CREST, Japan Science and Technology, 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551

[†]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577

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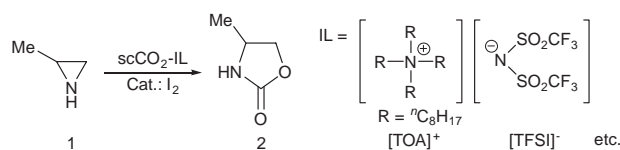
The hybrid reaction system composed of supercritical carbon dioxide and room temperature ionic liquid based on symmetric tetraalkyl ammonium salts can effectively promote the carbon dioxide fixation from aziridine to 2-oxazolidinone in the presence of iodine in high yield of 98% within 5 min. The TOF value under this condition is 254 times larger than that using conventional organic solvent.

From the standpoint of the environment protection, the development of production processes using chemical fixation of carbon dioxide (CO₂) has been drawing much interest in industrial chemistry and biotechnology, because there are numerous possibilities that CO₂ can be used as a safe and cheap C1 raw material to produce useful organic compounds. Supercritical carbon dioxide (scCO₂) possesses many advantageous properties such as tunable solubility, faster mass transfer than conventional organic solvent, controllability of reactions by pressure, and temperature manipulation. However, the CO₂ chemical fixation under scCO₂ conditions often needs longer reaction times extending to several hours to obtain satisfactory results so far, because of the inert property.¹

Recently, growing interest has been manifested in the use of room temperature ionic liquid (IL), which has been considered

“green solvent.” IL has a lot of advantages regarding environmental managements of the chemical synthesis.² However, IL has a fatal disadvantage for the difficulty in the separation of organic products and IL. To overcome the troublesome product-solvent separation, scCO₂-IL hybrid system was introduced as a greener system.³ This system can also be applied for the reaction such as the hydrogenation of styrene,⁴ the Beckman rearrangement of cyclohexanone oxime,⁵ and recently, we have reported the successful achievement of the rapid synthesis of cyclic carbonate using this hybrid reaction system based on imidazolium salts.⁶

In this paper, we have first applied the scCO₂-IL reaction system based on the tetraalkyl ammonium salts into the reaction of carbon dioxide with aziridine **1** into 2-oxazolidinone **2** (Scheme 1) to develop the various swift chemical fixation of CO₂, since the ILs are electrochemically more stable than that



Scheme 1.

Table 1. The carbon dioxide fixation from aziridine to 2-oxazolidinone under scCO₂-IL reaction system based on tetraalkyl ammonium salts

Run	Reaction time / min	Pressure / MPa	Reaction temp. / °C	Reaction system		Yield of 2 / %	Select. of 2 / %	TOF / h ⁻¹
1	5	10	40	[EMIM] ⁺ [BF ₄] ⁻	scCO ₂	0	0	0
2	5	10	40	[EMIM] ⁺ [TFSI] ⁻	scCO ₂	16	97	131
3	5	10	40	[TOA] ⁺ [TFSI] ^{-a}	scCO ₂	98	100	838
4	5	10	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	98	99	838
5	5	10	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	98	98	838
6	15	10	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	97	99	829
7	30	10	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	98	100	838
8	60	10	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	57	57	838 ^b
9	5	10	40	[TDA] ⁺ [TFSI] ^{-c}	scCO ₂	89	97	761
10	5	10	40	[TDA] ⁺ [TSAC] ^{-d}	scCO ₂	86	98	735
11	5	2	40	[TOA] ⁺ [TFSI] ⁻	CO ₂	2	98	17
12	5	8	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	64	99	547
13	5	14	40	[TOA] ⁺ [TFSI] ⁻	scCO ₂	57	98	487
14	360	11.8	40	Ethanol	scCO ₂	72	72	7.2
15	1260	6.9	80	Ethanol	CO ₂	44	— ^e	3.3

^a[TOA]⁺ is tetraoctyl ammonium cation, and [TFSI]⁻ is bis(trifluoromethylsulfonyl)imide anion.

^bAziridine **1** was not recovered, and unknown complex mixtures were formed.

^c[TDA]⁺ is tetradecyl ammonium cation.

^d[TSAC]⁻ is (2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide) anion.

^eWhen methanol was used as a solvent, the selectivity was 70% in Ref. 12c.

based on imidazolium salts.^{9a} The derivatives of 2-oxazolidinone⁷ **2** have been widely used in organic synthesis as chiral auxiliaries or building blocks for a variety of bioactive compounds.⁸ We found that the tetraalkyl ammonium salts with bis(trifluoromethylsulfonyl)imide cation⁹ is more effective for the chemical fixation than imidazolium salts.

The model reaction of CO₂ fixation from 2-methylaziridine **1** to 4-methyl-2-oxazolidinone **2** in the presence of iodine as a Lewis acid catalyst was conducted in a batch wise operation under scCO₂-IL reaction system with imidazolium salts or tetraalkyl ammonium salts in which iodine can be dissolved. The results were summarized in Table 1.¹⁰ Preliminary, 1-ethyl-3-methylimidazolium tetrafluoroborate([EMIM]⁺[BF₄]⁻) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM]⁺[TFSI]⁻) were used as a scCO₂-IL reaction system (Runs 1 and 2) for carbon dioxide fixation with aziridine **1**, but 4-methyl-2-oxazolidinone **2** was obtained in a very poor yield.

To attain the better yield, over 80% in a shorter reaction time, we applied the IL based on the tetraalkylammonium salts for the scCO₂-IL reaction system. When the tetraoctylammonium bis(trifluoromethanesulfonyl)imide([TOA]⁺[TFSI]⁻) is used, it is quite note worthy that the excellent yield of 98% was obtained within 5 min and at the low temperature of 40 °C (Run 3). The same reaction in ethanol at the temperature of 80 °C gave the lower yield of 44% for 21 h (Run 15),^{7a} and in ethanol-scCO₂ at 40 °C, the yield was 72% for 6 h (Run 14).¹¹ Furthermore, the turnover frequency (TOF) at 10 MPa (Run 3) is 838 h⁻¹, which is 116 times faster than that in previous report under the scCO₂ reaction system with ethanol as co-solvent (Run 14),¹¹ and surprisingly 254 times larger than that in conventional organic solvent (Run 15).^{7a} Besides, the IL can be used for recycling of the scCO₂-IL reaction system (Runs 4 and 5). Though this scCO₂-IL reaction system yields the excellent productivity even at shorter reaction time, unknown reactions, which might be the polymerization, occurred after longer reaction time leading to the decreasing of the yield of oxazolidinone (Runs 3 and 6–8).^{1a,12}

The pressure dependence of the yield of **2** was further investigated at 2, 8, 10, and 14 MPa (Runs 3 and 11–13), and an interesting pressure dependence was observed. The yield increases with increasing pressure, reaching a maximum yield at around 10 MPa, and then decreases with increasing pressure up to 14 MPa. In the range of atmospheric pressure to 14 MPa, two phases consisted of CO₂ and IL phase can be seen, and in the low pressure range below 10 MPa, CO₂ would dissolve into IL phase, and the concentration of CO₂ in the IL phase is increased with increasing pressure, which, in turn, would increase the reaction rate. Furthermore, the CO₂ phase is transformed into the supercritical state over 8 MPa, and so, a mass transfer of product from IL phase to the scCO₂ phase expected to be accelerated, resulting in the excellent yield.

At the higher pressure of 10 MPa, **1** can be dissolved in the CO₂ phase from the IL phase, resulting the decreased mole fraction of substrate **1** in the IL phase. Then the substrate **1** which is in the CO₂ phase would not transformed into **2** anymore. Therefore, the yield is decreased at the higher pressures above 10 MPa.

In conclusion, we found that the hybrid reaction system consisted of scCO₂-symmetric aliphatic ammonium salts was more suitable than that of scCO₂-imidazolium salts for the carbon

dioxide fixation from aziridine **1** to 2-oxazolidinone **2**. It can successfully derive the rapid reaction with 98% yield within 5 min. Furthermore, the TOF values under this reaction system are 116 times larger than that of the scCO₂ reaction system and 254 times larger than that of the conventional organic solvents.

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- 10 The typical experimental procedure is as follows: propylene imine (3.0 mmol), iodine (0.1 mmol), and ionic liquid (1.0 mL) were charged into a 25-cm³ reactor at 40 °C, and CO₂ was introduced into the reactor using a high-pressure liquid pump and compressed to the desired pressure within 5 min. The reactions were started by stirring the mixture, continued for 5 min. After reaction, the reactor was cooled to 0 °C with ice and the pressure was released slowly. 2-Oxazolidinone was purified from the crude products by distillation and was analyzed by NMR. The yields of the product were determined by GC-MS.
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