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Synthesis of styrene carbonate from carbon dioxide and styrene oxide with various zinc halide-based ionic liquids

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Abstract

Various zinc halide-based ionic liquids were prepared from zinc halides and onium halides as catalysts for the synthesis of styrene carbonate (SC) from styrene oxide and carbon dioxide. The effects of the ionic liquid catalyst composition (types of onium cation and halide, onium cation/zinc ratio) and CO₂ pressure on the reaction were investigated. The effectiveness of the onium cation as the active catalyst component was in the order of tetrabutylammonium > 1-butylpyridinium > 1-butyl-3-methylimidazolium >> choline. The type of halide atom originating from the zinc salt affected the catalytic activity of the ionic liquid more significantly than that of the one originating from the onium salt. The onium cation/zinc ratio also affected the SC yield, but its manner was different depending on the type of onium cation. Influence of CO₂ pressure was not significant.

Keywords: styrene carbonate; styrene oxide; carbon dioxide; binary catalyst; cycloaddition.

1. Introduction

Carbon dioxide (CO₂) is recognized to be an abundant, cheap, recyclable and non-toxic carbon source, which can replace toxic chemicals such as phosgene, isocyanates or carbon monoxide. The synthesis of cyclic carbonate via cycloaddition of CO₂ to epoxide is one of effective routes for the chemical fixation of CO₂. The five-membered cyclic carbonates are finding more extensive chemical applications as solvents, selective reagents, fuel additives, and monomers for polymers and intermediates in the production of pharmaceuticals and fine chemicals [1, 2]. Although the synthesis of cyclic carbonate from CO₂ and epoxides was applied in industrial scales [3], a number of works have been reported in the literature for the development of various catalyst systems, as already reviewed by several authors [4–10]. Among the catalysts reported so far, zinc complexes were found to have good activities for the CO₂ cycloaddition under mild conditions [11–18]. It was also found that the zinc halide and zinc oxide in conjunction with various bases provided efficient binary catalyst systems for the CO₂ cycloaddition, although these zinc compounds themselves had no activity for the reaction and the activities of the bases were very low [19–32]. This synergetic effect was attributed to cooperative activation of epoxide molecules by zinc atom (Lewis acid) and the base. Recently, the present authors found that various zinc halide-based ionic liquids containing different onium cations of tetraalkylammonium, dialkylimidazolium, alkylpyridinium and choline can be prepared by a simple heat treatment of mixtures of zinc halides and corresponding onium halides [33]. Among them, only dialkylimidazolium zinc tetrahalide ionic liquids were reported to be good catalysts for the CO₂ cycloaddition [14]; however, it is unknown whether the other zinc halide-based ionic liquids are also active for this reaction and the type of the onium cation affects the activity of the ionic liquid.

In the present study, various zinc halide based ionic liquids containing 1-butyl-3-methylimidazolium ([BMIM]), 1-butylpyridinium ([BPY]), tetrabutylammonium

([TBA]) and choline ([CHOL]) cations have been prepared from zinc halides and corresponding onium halides (Scheme 1), and used for the synthesis of styrene carbonate (SC) from CO₂ and styrene oxide (SO) (Scheme 2). Effects of types of onium cations and halides, the molar ratio of onium cation to zinc, and CO₂ pressure on the carbonate yield have been investigated.

Scheme 1

Scheme 2

2. Experimental

1-Butyl-3-methylimidazolium halides ([BMIM]Y, Y = Cl, Br), 1-butylpyridinium bromide ([BPY]Br) and choline chloride ([CHOL]Cl) were purchased from Aldrich Chemical Co. Tetrabutylammonium halides ([TBA]Y, Y = Cl, Br, I), zinc halides (ZnX₂, X = Cl, Br, I) and styrene oxide were purchased from Wako Pure Chemicals Ind. These chemicals were used without further purification.

In the present study various ionic liquids of the general formula, [L]_nZnX₂Y_n, were prepared from zinc halides and organic halides, where L, n, X and Y represent the onium cation involved in the ionic liquid ([BMIM], [BPY], [TBA] or [CHOL] in Scheme 1), the molar ratio of the organic cation to zinc cation (L/Zn), the halide atom originating from the zinc salt and that from the organic salt used for the preparation, respectively. In a typical procedure for the preparation of zinc based ionic liquid, ZnBr₂ (0.25 mmol) was mixed with the desired amount of [TBA]Br (0.5 mmol) in a glass flask, and heated to 140°C in air with stirring. The mixture was stirred at this temperature for 2 h. During the heat treatment, the mixture of the solids changed to homogeneous liquid of [TBA]₂ZnBr₂Br₂. Other ionic liquids were also prepared in the same way. For several runs, the value of n (L/Zn) was changed.

The reaction of styrene oxide (SO) and CO₂ was conducted batchwise in a 50 cm³ autoclave. The zinc based ionic liquid catalyst (0.1 mmol) and SO (35 mmol) were charged into the reactor. The reactor was purged with CO₂ three times and pressurized with CO₂ to 4 MPa. The reaction mixture was heated to 80°C and kept for 30 min at this temperature under stirring. The initial pressure of CO₂ at 80°C reached to 5 MPa. After the reaction, the reactor was cooled by ice water to room temperature and depressurized to an atmospheric pressure. The reaction mixture was added with 1 cm³ of toluene as an internal standard for analysis, diluted with ethyl acetate to 25 cm³ and analyzed on a gas chromatograph (Shimadzu 390B) packed with a capillary column (GL Science TC-17) using a flame ionization detector. The SO conversion and the SC yield were determined on the basis of the results obtained with authentic samples.

3. Results and Discussion

In the present study, various ionic liquids, [L]_nZnX₂Y_n, were prepared from zinc halides and onium halides as the catalysts for the SC synthesis. Under the present reaction conditions, 100% selectivity to SC was obtained in all the reaction runs.

3.1. Influence of ionic liquid composition on the SC synthesis

Table 1 shows the influence of the kind of organic cation on the SC yield. Among the tetrabromide ionic liquids (entries 1-3), the SC yield was in the order of [TBA]₂ZnBr₂Br₂ > [BPY]₂ZnBr₂Br₂ > [BMIM]₂ZnBr₂Br₂. The same order of the SC yield was obtained with dibromodichloride ionic liquids (entries 4-6), although the difference of the yield between [TBA] and [BPY] was small. Because the ionic liquid involving [CHOL] could be obtained only at n values below 0.67, the SC yield with [CHOL]_{0.67}ZnBr₂Cl_{0.67} was compared with that with [BMIM]_{0.67}ZnBr₂Cl_{0.67}. The SC yield with the former ionic liquid was much lower than that with the latter (entries 7, 8). Thus, the effectiveness of the onium cations as the active

catalyst component is in an order of [TBA] > [BPY] > [BMIM] >> [CHOL]. It should be noted that an excellent yield was obtained with [TBA]₂ZnBr₂Br₂ under mild conditions for a short reaction time of 30 min.

Table 1

The two [TBA]₂ZnX₂Y₂ and [BMIM]₂ZnX₂Y₂ catalyst systems were selected for further experiments to study the effects of the catalyst composition on the reaction. Table 2 lists the SC yields obtained with the ionic liquids containing various halide anions. When ZnBr₂ and [TBA]Y (Y = Cl, Br, I) were used as the catalyst precursors, the counter anion of the TBA salt employed had no effect on the carbonate yield (entries 1-3). Similar to this, when ZnI₂ and ZnCl₂ were used as the catalyst precursors, the SC yield did not depend on the counter anion of TBA salts used so much (entries 5-8). Exceptions were [TBA]₂ZnI₂I₂ and [TBA]₂ZnCl₂Cl₂ (entries 4, 9), and these ionic liquids gave much lower SC yields compared to the other ones. On the other hand, when the catalyst precursor of the onium salt was fixed to [TBA]I or [TBA]Br and the zinc halide precursor was changed, the order of the catalyst activity according to the zinc halide used was in the order of ZnBr₂ > ZnI₂ > ZnCl₂ (entries 1, 4, 7 and entries 2, 5, 8). This order changed to ZnBr₂ > ZnCl₂ > ZnI₂, when [TBA]Cl was used instead of [TBA]Br (entries 3, 6, 9). It should be noted that [TBA]₂ZnBr₂Cl₂ was more active than [TBA]₂ZnCl₂Br₂, although the chemical compositions of these ionic liquids were the same. Explanation for the reaction results represented in Table 2 is difficult at present; however, it can be said that the type of halide (X) originating from the zinc salt precursor is more significant than that of halide (Y) originating from TBA salt for determining the catalytic activity of the ionic liquid prepared.

Table 2

Similar examination was also made for ionic liquids of $[\text{BMIM}]_2\text{ZnX}_2\text{Y}_2$ (Table 3). Ionic liquids prepared from ZnI_2 gave almost the same SC yields with those prepared from ZnBr_2 , while the yields obtained with the ionic liquids prepared from ZnCl_2 were lower than the others. The influence of halide X of $[\text{BMIM}]_2\text{ZnX}_2\text{Y}_2$ is different from that of $[\text{TBA}]_2\text{ZnX}_2\text{Y}_2$. However, it can be said again that the halide X is more significant than the halide Y for determining the catalytic activity of the ionic liquids (entries 2 and 5).

Table 3

Figure 1 illustrates the influence of the molar ratio of organic cation to zinc ($n = [\text{L}]/\text{Zn}$) on the SC yields with $[\text{TBA}]_n\text{ZnBr}_2\text{Br}_n$ and $[\text{BMIM}]_n\text{ZnBr}_2\text{Br}_n$. When $[\text{TBA}]_n\text{ZnBr}_2\text{Br}_n$ was used as the catalyst, the SC yield increased with increasing the ratio from 1 to 2; however, further increase in the ratio did not increase the SC yield so much. Thus, the optimum ratio is 2 for $[\text{TBA}]_n\text{ZnBr}_2\text{Br}_n$. On the other hand, when $[\text{BMIM}]_n\text{ZnBr}_2\text{Br}_n$ was used as the catalyst, increase in the SC yield was observed with increasing the ratio up to 4. Thus, the influence of the ratio depends on the onium cation contained in the ionic liquid.

Fig. 1

3.2. Comparison of various catalyst systems for the SC synthesis

For comparison, ZnBr_2 or $[\text{TBA}]\text{Br}$ alone and a physical mixture of them ($[\text{TBA}]\text{Br}/\text{ZnBr}_2$) were used for the reaction. The results obtained are listed in Table 4. ZnBr_2 alone had no activity for the reaction and $[\text{TBA}]\text{Br}$ alone showed a very low activity (entries 1, 2). The SC yield was greatly improved by combination of ZnBr_2 and $[\text{TBA}]\text{Br}$ (entry 3); however, the SC yield obtained with the ionic liquid of $[\text{TBA}]_2\text{ZnBr}_2\text{Br}_2$ (entry 4) exceeded that obtained with the mixture system. In the catalyst system of the physical mixture, ZnBr_2

(Lewis-acid) and [TBA]Br (Lewis-base) are considered to activate SO molecules cooperatively, resulting in high SC yields [19]. Similarly, the ionic liquid catalyst would have bi-functionality. When [BMIM]Br and [BPY]Br were used instead of [TBA]Br, similar results were obtained, as shown in Table 4 (entries 5-10).

Table 4

3.3. Influence of CO₂ pressure on SC yield

Figure 2 shows the dependence of the SC yield with [TBA]₂ZnBr₂Br₂ on CO₂ pressure. The SC yield was enhanced by increasing the CO₂ pressure from 1 to 5 MPa. Above 5 MPa, the yield decreased slightly. Hence, so high CO₂ pressure is not required to get high SC yields. The phase behavior of the reactant mixture was previously investigated under the same conditions as employed in the present study, except for the catalyst used [20, 23]. It consisted of two phases; a CO₂-rich gas phase and a liquid phase, up to 14 MPa. The volume of the liquid phase decreased with increasing CO₂ pressure above 8 MPa. Around 16 MPa, CO₂ and the liquid phase took the form of a homogeneous phase. The solubility of the ionic liquid in the dense CO₂ gas phase, which is one of important factors determining the rate of reaction, is unknown. However, it is less likely to dissolve in the CO₂ gas phase. In addition, CO₂ can be soluble in the styrene oxide liquid phase. Hence, the reaction mainly occurs in the liquid phase, in which the substrate, the catalyst and CO₂ exist. The concentration of CO₂ in the liquid phase would be enhanced by increasing the pressure. Probably, this would cause the increase in the SC yield observed below 5 MPa. On the other hand, under supercritical conditions (> 7.4 MPa), dense phase CO₂ may dissolve a part of SO, resulting in the slight decrease of the SC yield observed above 8 MPa.

Fig. 2

3.4. Mechanistic considerations on the catalytic performance of zinc based ionic liquid

As described above (Table 2), among the ionic liquids of $[\text{TBA}]_2\text{ZnBr}_2\text{Y}_2$ ($\text{Y} = \text{Cl}, \text{Br}, \text{I}$), the type of halide Y had no effect on the SC yield. In contrast to this, when ZnBr_2 was physically mixed with $[\text{TBA}]\text{Y}$ halides and used for the SC production, the SC yield was in the order of $[\text{TBA}]\text{I} > [\text{TBA}]\text{Br} > [\text{TBA}]\text{Cl}$ [23]. These observations suggest that the catalytic function of the halide anion originating from the onium salt in the mixed catalyst system is different from that in the present ionic liquid system. Kim et al. prepared a solid sample of $[\text{1,3-dimethylimidazolium}]_2\text{ZnBr}_2\text{Cl}_2$ and analyzed its structure by a single crystal X-ray diffraction analysis [14]. They found that two dimethylimidazolium cations were paired with a dibromodichloro zincate dianion. Probably, the similar tetrahalide zincate anion would also be involved in the ionic liquid of $[\text{L}]_2\text{ZnX}_2\text{Y}_2$ prepared in the present study. This could be one of reasons for the difference in the halide effects on the SC yield between the present zinc based ionic liquid systems and the physically mixed ZnBr_2 and $[\text{TBA}]\text{Y}$ systems.

As shown in Table 4, high SC yields were obtained by the combination of ZnBr_2 and $[\text{TBA}]\text{Y}$. This could be ascribed to cooperative activation of epoxide molecules as proposed in many works for the cyclic carbonate synthesis with acid-base bi-functional catalyst systems [15, 17, 20–23, 26, 31, 32, 34–36]. The acid attacks the oxygen atom of the epoxide ring, while the base attacks the less sterically hindered carbon atom to open the ring. The zinc based ionic liquid would have similar bi-functionality. Zinc and halide atoms simultaneously attack the oxygen atom and the less sterically hindered carbon atom of the epoxide ring, respectively, resulting in the formation of a ring-opening product.

Scheme 3

Among the reactions involved in the catalytic cycle of the SC synthesis, the CO_2 insertion can be supposed to proceed easily under the present reaction conditions, because a few studies

reported that the insertion of CO₂ into metal–O bond of metal complexes occurred even around room temperature and at ambient pressure of CO₂ [11, 13, 37–39]. This might be a possible reason why the influence of CO₂ pressure on the SC yield was not so significant (Fig. 2). The dependence of the SC yield on the type of halide anion involved in the ionic liquid is complicated to explain. Probably, this would result from two conflicting factors of the nucleophilicity and the steric hindrance of the halide anion that participates to the cooperative activation of the epoxide molecule. As shown in Tables 2 and 3, the type of halide X was more significant than that of halide Y for determining the catalytic activity of the ionic liquid. Considering this, one can speculate that the participation of X is more significant than Y in the ring-opening step that is important for the overall reaction rate. The liberation of Y cannot be completely excluded, but its possibility would be low.

The structure of onium cation was significant for the catalytic activity of the ionic liquid (Table 1). Probably, the easiness of the liberation of halide species and/or the stability of the reaction intermediates would depend on the onium cation structure.

If two epoxide molecules are simultaneously coordinated to one molecule of zinc halide based ionic liquid and the reaction proceeds at the both sides, this can explain the optimum n value of 2 for the reaction with [TBA]_nZnBr₂Br_n. At larger n values, the increase of the yield was marginal. Similar proposal was made in a few studies using zinc halide based catalyst systems for the CO₂ cycloaddition to epoxide [20, 23, 25, 30, 31]. With [BMIM]_nZnBr₂Br_n, however, the SC yield increased up to the n value of 4. The conclusive explanation for this is difficult at present, but the easiness of the liberation of [BMIM]X may be increased with increasing the n value.

4. Conclusions

Various zinc halide based ionic liquids, [L]_nZnX₂Y_n, were prepared from zinc halides and

onium halides as the catalysts for the SC synthesis from SO and CO₂. The effectiveness of the onium cation as the active catalyst component was in the order of [TBA] > [BPY] > [BMIM] >> [CHOL]. The type of halide atom originating from the zinc salt affected the catalytic activity of the ionic liquid more significantly than that of the one originating from the onium salt. The onium cation/zinc ratio (n) also affected the SC yield, but its manner was different depending on the type of onium cation. The optimum n value was 2 for [TBA]_nZnBr₂Br_n. At larger values of n, the increase in the SC yield was marginal. With [BMIM]_nZnBr₂Br_n, however, the yield increased with the n value up to 4. Influence of CO₂ pressure was not significant.

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Captions for tables, schemes and figures.

Table 1 Synthesis of styrene carbonate from CO₂ and SO with various ionic liquids containing different organic cations.

Table 2 Effects of types of halides contained in [TBA]₂ZnX₂Y₂ on SC yield from CO₂ and SO.

Table 3 Effects of types of halides contained in [BMIM]₂ZnX₂Y₂ on SC yield from CO₂ and SO.

Table 4. Synthesis of styrene carbonate from CO₂ and SO with various catalyst systems.

Scheme 1. Synthesis of styrene carbonate from CO₂ and styrene oxide.

Scheme 2. Ionic liquids prepared from zinc halides and onium halides as catalysts for the synthesis of styrene carbonate.

Fig. 1. Effects of the molar ratio of organic cation to zinc on SC yields with (●) [TBA]_nZnBr₂Br_n and with (□) [BMIM]_nZnBr₂Br_n. Reaction conditions: [TBA]_nZnBr₂Br_n, 0.025 mmol; [BMIM]_nZnBr₂Br_n, 0.1mmol; SO, 35 mmol; CO₂, 5 MPa ; temperature, 80°C; time, 30 min.

Fig. 2. Dependence of SC yield on CO₂ pressure. Reaction conditions: [TBA]₂ZnBr₂Br₂, 0.05 mmol; SO, 35 mmol; temperature, 80°C; time, 30 min.

Table 1 Synthesis of styrene carbonate from CO₂ and SO with various ionic liquids containing different organic cations.

Entry	Catalyst	SC yield (%)
1	[TBA] ₂ ZnBr ₂ Br ₂	94
2	[BPY] ₂ ZnBr ₂ Br ₂	77
3	[BMIM] ₂ ZnBr ₂ Br ₂	71
4	[TBA] ₂ ZnBr ₂ Cl ₂	70
5	[BPY] ₂ ZnBr ₂ Cl ₂	68
6	[BMIM] ₂ ZnBr ₂ Cl ₂	47
7	[BMIM] _{0.67} ZnBr ₂ Cl _{0.67}	31
8	[CHOL] _{0.67} ZnBr ₂ Cl _{0.67}	5

Reaction conditions: Catalyst, 0.1 mmol; SO, 35 mmol; CO₂, 5 MPa; temperature, 80°C; time, 30 min.

Table 2 Effects of types of halides contained in $[\text{TBA}]_2\text{ZnX}_2\text{Y}_2$ on SC yield from CO_2 and SO.

Entry	Halide (X_2Y_2)	SC yield (%)
1	Br_2I_2	82
2	Br_2Br_2	81
3	Br_2Cl_2	83
4	I_2I_2	32
5	I_2Br_2	68
6	I_2Cl_2	61
7	Cl_2I_2	59
8	Cl_2Br_2	70
9	Cl_2Cl_2	33

Reaction conditions: Catalyst, 0.05 mmol; SO, 35 mmol; CO_2 , 5 MPa; temperature, 80°C; time, 30 min.

Table 3 Effects of types of halides contained in [BMIM]₂ZnX₂Y₂ on SC yield from CO₂ and SO.

Entry	Halide (X ₂ Y ₂)	SC yield (%)
1	Br ₂ Br ₂	71
2	Br ₂ Cl ₂	66
3	I ₂ Br ₂	75
4	I ₂ Cl ₂	68
5	Cl ₂ Br ₂	47
6	Cl ₂ Cl ₂	10

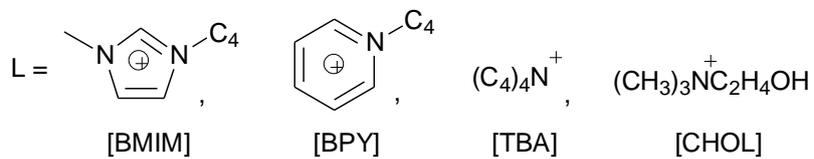
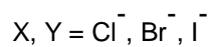
Reaction conditions: Catalyst, 0.1 mmol; SO, 35 mmol; CO₂, 5 MPa ; temperature, 80°C; time, 30 min.

Table 4. Synthesis of styrene carbonate from CO₂ and SO with various catalyst systems.

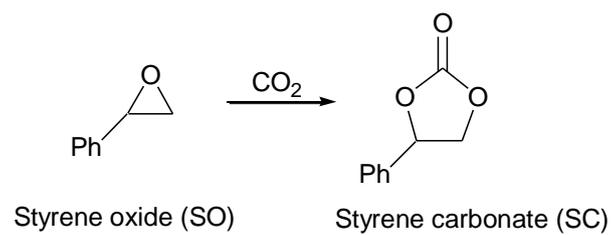
Entry	Catalyst	SC yield (%)
1	ZnBr ₂	0
2	[TBA]Br	12
3	[TBA]Br/ZnBr ₂ ^a	69
4	[TBA] ₂ ZnBr ₂ Br ₂	94
5	[BMIM]Br	10
6	[BMIM]Br/ZnBr ₂ ^a	56
7	[BMIM] ₂ ZnBr ₂ Br ₂	66
8	[BPY]Br	11
9	[BPY]Br/ZnBr ₂ ^a	70
10	[BPY] ₂ ZnBr ₂ Br ₂	77

Reaction conditions: ZnBr₂, 0.1 mmol; onium bromide 0.2 mmol; ionic liquid, 0.1 mmol; SO, 35 mmol; CO₂, 5 MPa; temperature, 80°C; time, 30 min.

^a A mixture of ZnBr₂ and onium bromide was used for the reaction.



Scheme 1. Ionic liquids prepared from zinc halides and onium halides as catalysts for the synthesis of styrene carbonate.



Scheme 2. Synthesis of styrene carbonate from CO₂ and styrene oxide.

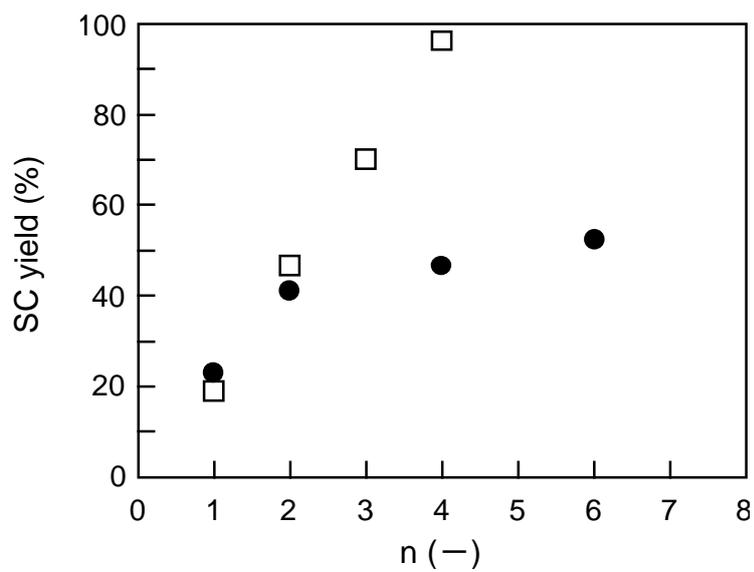


Fig. 1. Effects of the molar ratio of organic cation to zinc on SC yields with (●) $[\text{TBA}]_n\text{ZnBr}_2\text{Br}_n$ and with (□) $[\text{BMIM}]_n\text{ZnBr}_2\text{Br}_n$. Reaction conditions: $[\text{TBA}]_n\text{ZnBr}_2\text{Br}_n$, 0.025 mmol; $[\text{BMIM}]_n\text{ZnBr}_2\text{Br}_n$, 0.1mmol; SO, 35 mmol; CO₂, 5 MPa ; temperature, 80°C; time, 30 min.

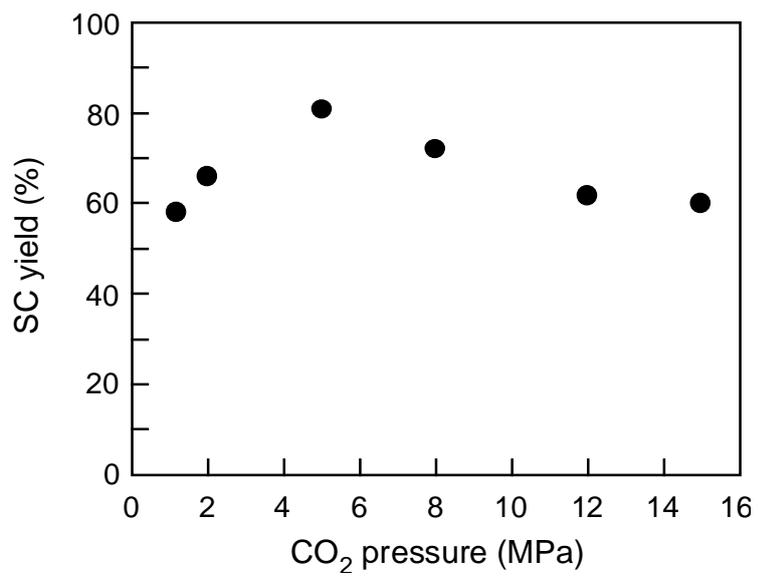


Fig. 2. Dependence of SC yield on CO₂ pressure. Reaction conditions: [TBA]₂ZnBr₂Br₂, 0.05 mmol; SO, 35 mmol; temperature, 80°C; time, 30 min.