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Synthesis of 1,3-dialkylurea from ethylene carbonate and amine using calcium oxide

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Abstract

Several basic metal oxide catalysts were tested for the synthesis of 1,3-disubstituted urea from ethylene carbonate (EC) and amine. Among the catalysts used, CaO has been found to be an excellent recyclable catalyst for the reaction. It has been suggested that strongly basic property of CaO results in its high activity. Disubstituted ureas are obtained from propylamine and butylamine with high yields at 100 °C. Slightly higher reaction temperatures are necessary for obtaining good yields from amines having larger molecular weights and urea is not produced from dibutylamine as a secondary amine. Propylene carbonate can be used instead of EC for the reaction. A reaction mechanism was proposed, which involves reaction between EC and amine giving a carbamate followed by catalytic reaction between the carbamate and amine, yielding 1,3-disubstituted urea. It is suggested that the latter reaction is the rate-determining step. On the basis of this reaction mechanism, the synthesis of unsymmetric urea was also examined. 2-Hydroxyethyl butylcarbamate is selectively produced from EC with butylamine in the absence of the catalyst at a low temperature and reacts with benzylamine producing 1-butyl-3-benzylurea along with symmetric dialkyl ureas.
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Keywords: Solid base catalyst; Calcium oxide; Cyclic carbonate; Dialkyl urea; Carbamate

1. Introduction

In conventional base-catalyzed organic syntheses, homogeneous catalysts such as alkali alkoxide and organic amine are used. However, they have drawbacks in catalyst–product separation, regeneration, etc. Solid base catalysts are inexpensive and are more easily separable and recyclable than the homogeneous catalysts [1–5]. Hence, the use of solid base catalysts is desirable from the viewpoints of economy and green chemistry and is gaining much attention. However, little effort has been given to the study of solid base catalysts in contrast to extensive study of solid acid catalysts [1–5].

1,3-Disubstituted ureas have found extensive applications such as dyes, antioxidants, corrosion inhibitor, and intermediates for the preparation of pharmaceuticals and agricultural chemicals [6]. They can be synthesized from amines via phosgenation [7], reductive carbonylation [8–13] or oxidative carbonylation [14–20]; however, these reactions are not eco-friendly due to risks associated with the use of the poisonous compounds of phosgene and carbon monoxide and/or a potentially explosive mixture of carbon monoxide and oxygen. The reactions of amine with bis(4-nitrophenyl) carbonate [21], diethyl carbonate [22,23] and dimethyl carbonate [23–27] produce corresponding 1-substituted carbamates. These compounds can further react with amines producing corresponding 1,3-disubstituted ureas [21,28,29]. However, these carbonates are produced via similar hazardous routes of phosgenation or oxidative carbonylation [21,30–32]. Reactions of carbon dioxide with amines also produce disubstituted ureas [33–38]. These reactions are attractive, but expensive dehydrating reagents such as carbodiimides and organophosphites are indispensable for getting high yields [33–36]. A few catalyst systems that do not require any dehydrating reagents have been reported [37,38]; however, the reaction rates are not so fast.

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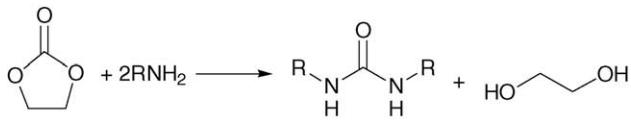


Scheme 1. Synthesis of 1,3-disubstituted urea from ethylene carbonate and amine.

Another way to synthesize 1,3-disubstituted urea is the reaction of amine and ethylene carbonate (EC) in the presence of base catalysts (Scheme 1). This reaction could be an EC based carbon dioxide fixation to important chemicals, since EC is synthesized in a large amount via the reaction of ethylene oxide and carbon dioxide. In a recent preliminary paper, we have first reported that calcium oxide is a good solid catalyst for the syntheses of disubstituted ureas from EC and primary amines [39]. Good yields are obtained with CaO under mild conditions and these values are comparable to those obtained with homogeneous base catalysts such as sodium methoxide and trialkyl amines [40]. In the present paper, a detailed study is reported.

2. Experimental

Catalysts of CaO, ZnO, ZrO_2 and MgO were used. CaO, ZnO and ZrO_2 were prepared by decomposition of calcium hydroxide at 550 °C for 4 h, hydroxy zinc carbonate at 350 °C for 4 h and zirconium oxynitrate at 500 °C for 3 h, respectively. MgO was a commercially available reagent and used without any pretreatments. BET surface areas of CaO, ZnO, ZrO_2 and MgO thus obtained were 13, 49, 49 and 14 m^2/g, respectively. As a control, a homogeneous base catalyst of sodium methoxide was also used for the reaction. The calcined catalyst samples were kept in a desiccator using glass bottles filled with argon gas.

The reaction was performed in a 50 mL stainless steel autoclave equipped with a mechanical agitator. After 40 mmol of ethylene carbonate, 80 mmol of amine (propylamine, butylamine, hexylamine, cyclohexylamine, benzylamine, aniline) and 0.5 g of the catalyst were charged into the reactor, the reactor was heated to the desired reaction temperatures and kept for 1 or 3 h. After the reaction, the reactor was cooled to room temperature and the reaction mixture was dispersed in 50 mL of a solvent, which was water for the experiments with propylamine and butylamine, ethanol for that with cyclohexylamine and acetone for those with the other amines. Then, the resulting mixture was stirred for 1 h at room temperature. The solid formed was filtered off and washed with the solvent. The product yield was determined from the weight of the solid by subtracting the catalyst weight. The product was characterized by gas chromatography, mass spectrometry, melting point measurements, and ^{1}H NMR; comparison with authentic samples was made whenever possible. In several runs using butylamine, the reaction was carried out for several periods of time, the reaction mixture was dissolved in acetone and its composition was determined by gas chromatography. In catalyst recycling runs, the product was dissolved in DMF. Then, the catalyst was separated by filtration, washed with acetone, dried under vacuum, and used for the next run.

Synthesis of unsymmetric urea was also investigated. After 40 mmol of EC and 40 mmol of butylamine (amine 1) were charged in the rector, the reactor was heated to 70 °C and kept for 2 h. After the reaction, the reactor was cooled to room temperature, to the reaction mixture were added 40 mmol of benzylamine (amine 2) and 0.5 g of CaO, and then the mixture was heated to 125 °C and kept for 3 h. After the reaction, the resulting reaction mixture was treated as described above using acetone as a solvent. In a reverse manner, experiments using benzylamine as amine 1 and butylamine as amine 2 were also conducted.

Basic properties of the catalysts were measured by temperature programmed desorption (TPD) of adsorbed CO_2 using a conventional flow reactor. After a stream of 20 vol.% CO_2–He mixture was passed over 0.25 g of the catalyst at room temperature for 20 min, gases in the reactor were flushed with a helium stream. Then, the temperature was ramped at a heating rate of 10 K/min to 800 °C. The effluent from the reactor was analyzed by gas chromatography or mass spectrometry.

3. Results and discussion

Several metal oxide catalysts were used for the 1,3-dibutylurea synthesis from ethylene carbonate (EC) and butylamine. Table 1 lists the reaction results obtained with those catalysts along with that with sodium methoxide. It is seen that among the catalysts used only CaO is a good catalyst. 1,3-Dibutylurea is obtained in a yield of 49% after the reaction for 1 h with CaO (entry 1). When the reaction time is lengthened from 1 to 3 h, the yield increases from 49% to 78% (entry 2). In contrast to the reaction with CaO, ZnO gives a very poor yield (entry 3) and MgO and ZrO_2 do not produce the disubstituted urea (entries 4 and 5). Analysis of the aqueous phase used for the post-reaction procedures (see Section

Table 1
1,3-Dibutylurea synthesis using various catalysts[a]

Entry	Catalyst	Yield (%)	TOF (h^{-1})[b]
1	CaO	49	2.2 (109)[c]
2	CaO[d]	78	1.2 (58)[c]
3	ZnO	6	0.4
4	MgO	0	0
5	ZrO_2	0	0
6	CH_3ONa	79	3.4

[a] Catalyst, 0.5 g; EC, 40 mmol; butylamine, 80 mmol; temperature, 100 °C; time, 1 h.
[b] Moles of dibutylurea formed per mole of the catalyst per hour.
[c] Calculated using the numbers of surface active sites estimated from TPD of CO_2.
[d] The reaction was carried out for 3 h.

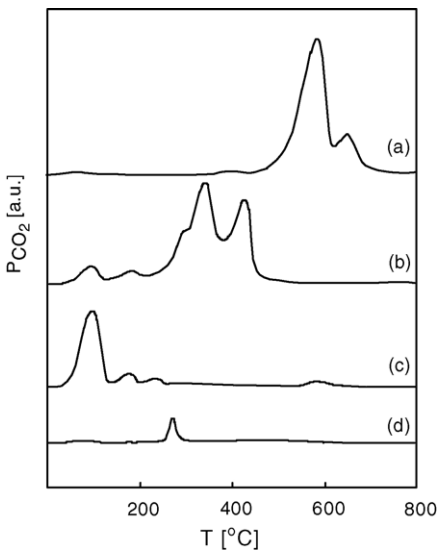


Fig. 1. TPD spectra of adsorbed CO_2 over (a) CaO; (b) MgO; (c) ZrO_2 and (d) ZnO.

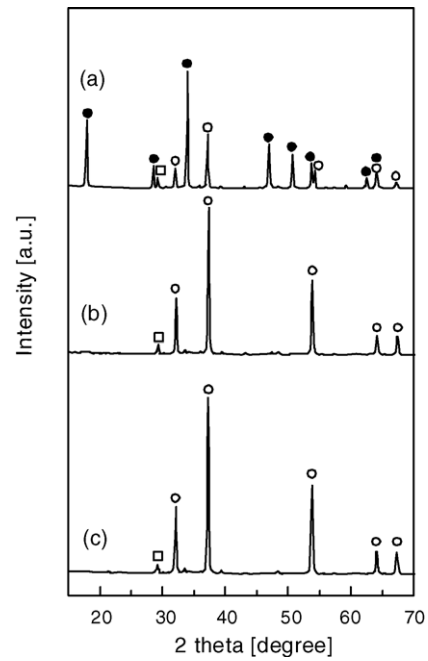


Fig. 2. XRD patterns of CaO obtained from $Ca(OH)_2$ by the calcination at (a) 450 °C; (b) 550 °C and (c) 650 °C for 4 h. (●) $Ca(OH)_2$; (◯) CaO; (□) $CaCO_3$.

2) showed that, with all of the catalysts listed in Table 1, all EC disappeared and 2-hydroxyethyl butylcarbamate were produced. The formation of the carbamate compound will be discussed later. The turnover frequency (TOF) based on total mole of CaO is 2.2 h^{-1} for the experiment of entry 1. On the other hand, a homogeneous base catalyst of sodium methoxide gives a TOF of 3.4 h^{-1} under the same conditions (entry 6). Thus, the apparent (low estimated) TOF for CaO is comparable with TOF for an effective homogeneous catalyst, sodium methoxide. The number of surface active sites of CaO is estimated to be 0.38 mmol/g from temperature programmed desorption (TPD) of adsorbed CO_2 as described below. TOF based on this amount of the surface active sites are 108 and 58 h^{-1} for entries 1 and 2, respectively. These (true) TOF values are much higher than that of sodium methoxide.

To elucidate the difference between the catalysts, basic properties of the catalysts were examined by TPD of adsorbed CO_2. The spectra are illustrated in Fig. 1. For CaO, CO_2 desorption peaks are observed at 585 and 650 °C. For ZnO and MgO, peaks appeared below 500 °C. ZrO_2 has a trace amount of CO_2 desorption at 580 °C. These results suggest that CaO has a larger amount of strongly basic sites compared with the other catalysts, resulting in its higher activity observed.

CaO catalysts were prepared from $Ca(OH)_2$ by calcination at various temperatures and used for the dibutylurea synthesis. Fig. 2 illustrates the XRD patterns of these catalysts prepared. A part of $Ca(OH)_2$ remains un-decomposed after the calcination at 450 °C. Above 550 °C, $Ca(OH)_2$ decomposes to CaO completely. Table 2 shows the yields of dibutylurea along with BET surface areas of the CaO catalysts. Although the difference in the yield is not so distinct, CaO calcined at 550 °C gives the highest dibutylurea yield. The lowest yield with CaO calcined at 450 °C could be owing to its low surface area and/or the incomplete decomposition of the $Ca(OH)_2$ precursor phase due to the low calcination temperature. Uncalcined $Ca(OH)_2$ was found to have no activity for the reaction. However, if the decomposition of the precursor proceeds according to a contracting sphere model, $Ca(OH)_2$ phase exists only inside of CaO bulk and, hence, surface of the sample calcined at 450 °C is covered with CaO phase. Thus, it is highly probable that the lowest yield with this catalyst would result from the lowest BET surface area. Although Fig. 2 shows the presence of a small amount of $CaCO_3$, pure $CaCO_3$ has been found to have no activity for the reaction. Hence, $CaCO_3$ existing in the samples has no contribution to the activity. On the basis of these results, further experiments were conducted with the CaO sample obtained by the calcination at 550 °C.

Table 3 shows the influence of the reaction temperature on the synthesis of dibutylurea. When the reaction temperature is increased from 100 to 125 °C, the yield of dibutylurea increases from 49% to 86%. However, further raising the reaction temperature does not cause increase in the yield.

Table 4 represents the results for the reactions of EC with various amines. It is seen that CaO is also effective for the synthesis of various disubstituted ureas. Propylamine and

Table 2
Influence of calcination temperature on BET surface area of CaO and its activity for the 1,3-dibutylurea synthesis

Temperature (°C)	BET area (m^2/g)	Yield (%)
450	6	53
550	13	78
650	11	70

Reaction conditions: CaO, 0.5 g; EC, 40 mmol; butylamine, 80 mmol; temperature, 100 °C; time, 3 h.

Table 3
Influence of reaction temperature on the 1,3-dibutylurea synthesis

Temperature (°C)	Yield (%)
100	49
125	86
150	83

Reaction conditions: CaO, 0.5 g; EC, 40 mmol; butylamine, 80 mmol; time, 1 h.

Table 4
Synthesis of 1,3-disubstituted ureas from EC with various amines

Entry	Amine	Temperature (°C)	Yield (%)
1	Propylamine	100	68
2	Butylamine	100	78
3	Hexylamine	125	77
4	Cyclohexylamine	125	35
5	Cyclohexylamine	150	59
6	Benzylamine	125	38
7	Benzylamine	150	55
8	Dibutylamine	125	0[a]
9	Aniline	125	0[b]

Reaction conditions: CaO, 0.5 g; EC, 40 mmol; amine, 80 mmol; time, 3 h.
[a] 2-Hydroxyethyl butylcarbamate and 2-dibutylamino-ethanol were formed.
[b] 2-Phenylamino-ethanol was formed.

butylamine give good yields for the corresponding disubstituted ureas at a reaction temperature of 100 °C (entries 1 and 2). It is noted that excess amine is not required under the present reaction conditions. This is more preferable from the viewpoint of economics. Slightly higher reaction temperatures are necessary for obtaining the substituted ureas from hexylamine, cyclohexylamine and benzylamine with good yields (entries 3, 5 and 7). However, no substituted urea is obtained from dibutylamine as a secondary amine (entry 8) and from aniline. Thus, CaO is usable for the reaction of EC with primary amines except for aniline.

For the reactions of various amines, propylene carbonate (PC) was used instead of EC (Table 5). The disubstituted ureas are obtained from PC and amines with good yields, which are almost the same as those from EC shown in Table 4. Thus, PC is also usable for the title reaction.

Recycling use of CaO was examined for the syntheses of some dialkylureas (Table 6). After being weighed, the product was dissolved in DMF. Then, the catalyst was separated by filtration, washed with acetone, dried under vacuum, and reused for a subsequent reaction run. When CaO is reused for dibutylurea synthesis, its activity disappears by recycling (entries 1 and 2). The urea is not obtained in the first recycling run. However, the deactivated catalyst can be regenerated by

Table 5
Synthesis of 1,3-disubstituted ureas from PC with various amines[a]

Entry	Amine	Temperature (°C)	Yield (%)
1	Butylamine	100	80
2	Hexylamine	125	52
3	Cyclohexylamine	150	64
4	Benzylamine	150	57

[a] CaO, 0.5 g; PC, 40 mmol; amine, 80 mmol; time, 3 h.

Table 6
Recycling of CaO for disubstituted urea synthesis[a]

Entry	Recyling	Amine (reaction temperature)	Yield (%)
1	0	Butylamine (100 °C)	49
2	1		0
3	2[b]		50
4	0	Hexylamine (125 °C)	77
5	1		73
6	0	Benzylamine (150 °C)	55
7	1		56
8	2		55
9	3		54

[a] CaO, 0.5 g; EC, 40 mmol; amine, 80 mmol; time, 1 h for butylamine and 3 h for the other amines.
[b] The catalyst was calcined at 550 °C for 1 h before the second recycling run.

re-calcination in air at 550 °C for 1 h (entry 3). Fig. 3 illustrates XRD patterns of CaO obtained before and after the first run (recycle 0) and after the re-calcination. It is seen that CaO is hydrated to $Ca(OH)_2$ after the reaction and $Ca(OH)_2$ produced is transformed to CaO again by the re-calcination. In the course of the post-reaction procedures, the reaction mixture containing the catalyst is treated in water (see Section 2). Furthermore, CaO is recyclable without re-calcination for the syntheses of dihexylurea and dibenzylurea, for which acetone is used instead of water in the course of the post-reaction procedures (entries 4–9). Hence, it is concluded that the water treatment during the post-reaction procedures causes the catalyst deactivation. However, it is clear that the catalyst deactivated with water can be regenerated by the calcination. It is noted that the procedures for the recycle runs were carried out under ambient atmosphere. Exposing solid base catalysts to air, even for short periods, sometimes causes their severe

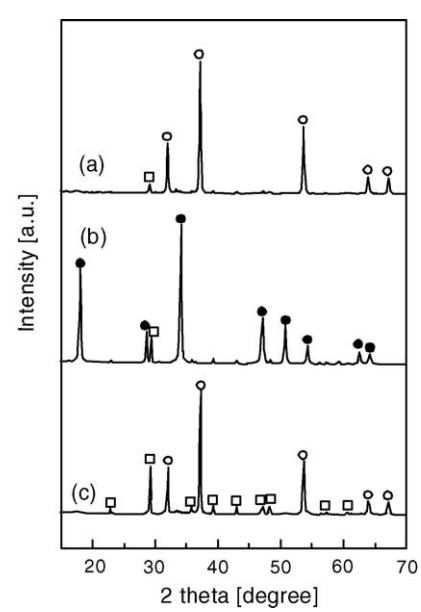


Fig. 3. XRD patterns of CaO (a) before and (b) after the reaction run (entry 1 in Table 6), and (c) after recalcination at 550 °C for 1 h before the second recycling. (◯) CaO; (●) $Ca(OH)_2$; (□) $CaCO_3$.

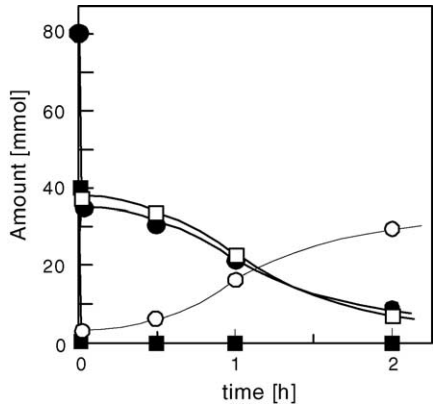
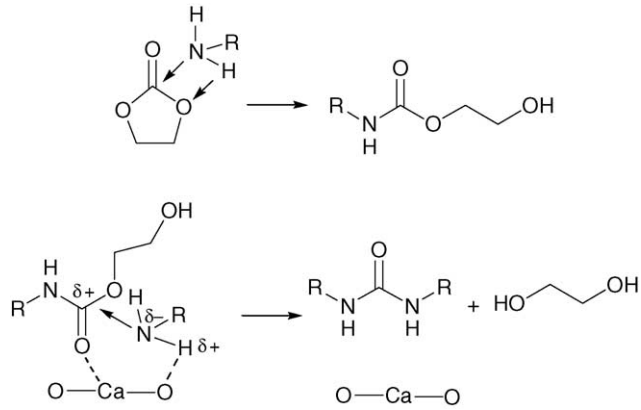


Fig. 4. Variation of the composition of the reaction mixture. (■) EC; (●) butylamine; (□) 2-hydroxyethyl butylcarbamate; (◯) dibutylurea. Reaction conditions: CaO, 0.5 g; EC, 40 mmol; butylamine, 80 mmol; temperature, 100 °C.



Scheme 2. Reaction mechanism for the synthesis of 1,3-disubstituted urea from EC and amine.

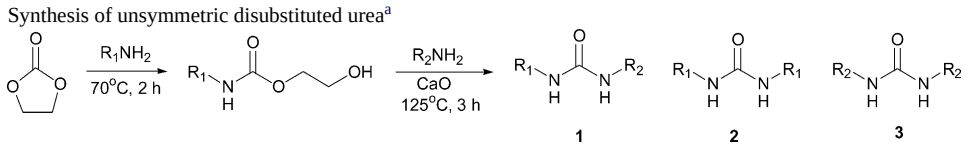
deactivation [1,3]. However, such deactivation was not observed for the present reaction system.

Dibutylurea synthesis was carried out for various periods of time. Fig. 4 illustrates change in the amounts of the substrates and the products with time. Within a few minutes, all EC and almost the same amount of butylamine are consumed. Simultaniously, 2-hydroxyethyl butylcarbamate is produced along with a small amount of dibutylurea and the amount of the carbamate formed is almost the same as that of EC consumed. Then, the amounts of both butylurea remaining and the carbamate slowly decrease with time and that of dibutylurea increases gradually. On the basis of these results, a reaction mechanism for the title reaction has been proposed as illustrated in Scheme 2. EC reacts with one molecule of amine, being transformed to 2-hydroxyethyl alkylcarbamate. The carbamate further reacts with another amine molecule, producing ethylene glycol and 1,3-dialkylurea. The variations of the substrates and products amounts with time strongly suggest that the second reaction of carbamate and amine is the rate-determining step for dibutylurea formation. Kaupp et al. [41] reported that methylamine and ethylamine rapidly react with EC around room temperature without any catalyst, producing corresponding 2-hydroxyethyl alkylcarbamates with high yields. Moreover, in a separate run in the absence of the catalyst, EC completely reacted with butylamine under the conditions for Fig. 4, producing the corresponding 2-hydroxyethyl butylcarbamate quantitatively. Hence, CaO may catalyze only the second step. Since it has been postulated that metal cation of basic metal oxide has Lewis acidity [1,3], the carbamate may be activated on this Lewis acidic sites.

As shown in Table 4, no substituted urea was obtained from dibutylamine and aniline. The products observed were 2-hydroxyethyl dibutylcarbamate and 2-dibutylamino-ethanol for the former amine and 2-(phenylamino)-ethanol for the latter amine. For the other amines, the formation of analogous aminoethanol products was not observed. When EC and dibutylamine were allowed to react at 70 °C for 2 h, about 60% of EC was converted to 2-hydroxyethyl dibutylcarbamate. Probably, the steric hindrance of two butyl groups should result in low reactivity of the carbamate to the amine, and hence, in the absence of the tetrasubstituted urea formation. In contrast, no reaction occurred between EC and aniline at 70 °C. This would be the reason why diphenylurea was not obtained from EC and aniline. Probably, the amino-ethanol compounds should be formed from the reactions of the amines with ethylene oxide, which can be produced via the decomposition of remaining EC [42,43].

On the basis of the reaction mechanism proposed, it is suggested that, if one kind of carbamate is produced from EC and one kind of amine (amine 1) and then further reacts with another kind of amine (amine 2), unsymmetric urea

Table 7
Synthesis of unsymmetric disubstituted urea[a]



Entry	Amine 1	Amine 2	Product (yield)[b]
1	Butylamine	Benzylamine	**1** (35%), **2** (10%), **3** (16%)
2	Benzylamine	Butylamine	**1** (11%), **2** (6%), **3** (2%)

[a] EC (40 mmol) was reacted with amine 1 (40 mmol) at 70 °C for 2 h and then carbamate formed was reacted with amine 2 (40 mmol) at 125 °C for 3 h using 0.5 g of CaO.
[b] Based on the amount of EC used.

would be synthesized. So, the synthesis of unsymmetric dialkylurea was examined. When 40 mmol of EC was allowed to react with 40 mmol of butylamine at 70 °C for 2 h in the absence of the catalyst, 99% of EC was selectively converted to 2-hydroxyethyl butylcarbamate. After cooling, to this reaction mixture were added 40 mmol of benzylamine and CaO and then the mixture was heated to 125 °C and kept for 3 h. As Table 7 shows, 1-butyl-3-benzylurea **1** is formed by these procedures; however, dibutylurea **2** and dibenzylurea **3** are also produced (entry 1). Probably, transamination should occur between the carbamate and benzylamine and/or between the urea and the amine. In a reverse manner, 2-hydroxyethyl benzylcarbamate was selectively synthesized from EC and benzylamine and further allowed to react with butylamine using CaO (entry 2). In this case, the three kinds of disubstituted ureas are also produced, but their yields are lower than those from butylcarbamate. The conversion of EC for the reaction with benzylamine was 92%, which is almost the same as that for the reaction between EC and butylamine; i.e. the amounts of the carabamates formed are almost the same in both cases. Hence, the lower yields of the ureas suggest the lower reactivity of 2-hydroxyethyl benzylcarbamate than 2-hydroxyethyl butylcarbamate. The structure of the alkyl group attached to the nitrogen atom of carbamate may affect the reactivity of the carbamate.

4. Conclusion

The present paper shows that CaO is an excellent catalyst for the synthesis of 1,3-dialkyl ureas from EC and monoalkyl amines. It has been suggested that strongly basic property of CaO results in its high activity. Slightly higher reaction temperatures are necessary for obtaining good yields from amines having larger molecular weights. Propylene carbonate can be used instead of EC for the title reaction. A reaction mechanism has been proposed, in which a catalytic reaction of a carbamate and amine is the rate-determining step of the title reaction. 2-Hydroxyethyl butylcarbamate and 2-hydroxyethyl benzylcarbamate were selectively produced with high yields from EC with butylamine and benzylamine, respectively, in the absence of the catalyst at a low temperature. From these carbamates, unsymmetric urea is obtained along with symmetric ureas. The latter compounds may be formed via transamination. The structure of the alkyl group attached to the nitrogen atom of carbamate may affect the reactivity of the carbamate.

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