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A simple synthesis of ethylene carbonate from carbon dioxide and 2-chloroethanol using silica gel as a catalyst

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ABSTRACT

A “green”, simple, technically and economically feasible synthesis of valuable ethylene carbonate from 2-chloroethanol and CO₂ was developed using K₂CO₃ as a base, silica gel as a catalyst and under mild reaction conditions. The influence of reaction temperature, CO₂ pressure, base and additives on conversion of 2-chloroethanol was studied.

1. Introduction

Ethylene carbonate is used as a polar solvent for polymeric compounds [1,2], a reaction medium for a variety of chemical processes [3,4], an extractant [5], a plasticizer [6], a blowing agent [7], a stabilizer for lubricating oils [8], a high permittivity component of electrolytes in lithium batteries [9], precursor of biodegradable polyethylene carbonate [10]. Ethylene carbonate is generally produced by reaction of inflammable and carcinogenic ethylene oxide with carbon dioxide at a high temperature and high pressure [11,12]. The thus obtained ethylene carbonate contains some ethylene glycol admixtures derived from its raw materials. Ethylene carbonate also contains a trace amount of water in addition to the above impurity. Interestingly, it is reported that ethylene carbonate having low diol content is more useful in the capacity of the electrolytic solvent. Still, it is necessary that impurities contained in ethylene carbonate should be avoided [13].

With CO₂ levels increasing in the atmosphere, CO₂ has become an interesting building block in organic synthesis because of its low cost. Therefore, efforts to utilize CO₂ as a “green” reagent, rather than to consider it waste, continue to attract considerable attention [14]. Recently, it was reported that organic carbonates were successfully prepared from 1,2-halohydrins and CO₂ (20 atm) in polyethylene glycol using K₂CO₃ at 50 °C [15]. Hirose et al. succeeded in preparation of different five-membered carbonates from 1,2-halohydrins and CO₂

using K₂CO₃ in good-to-high yields under very mild reaction conditions (30 °C, 1 atm CO₂) in dry DMF [16], but this solvent has a high boiling point, forms strong hydrogen bonds with reaction products and, moreover, is highly hygroscopic.

In this study, we show that a cheap silica gel for column chromatography can efficiently promote conversion of 2-chloroethanol and CO₂ to valuable ethylene carbonate.

2. Experimental part

2.1. Materials

Silica gel (0.06–0.2 mm, 60 Å, Acros Organics), 2-chloroethanol (99 + %), Na₂CO₃ (99 + %), K₂CO₃ (99 + %) are commercially available reagents (Acros Organics). CO₂ (99.99 % purity) was purchased from Voessen.

2.2. Typical catalytic experiments

The corresponding silica gel (25 mg), tetraalkylammonium halide 5 mg (if necessary, see in the Table 1), 2-chloroethanol (0.4 mL, 6 mmol) and base 6.6 mmol were introduced in a high pressure autoclave (10 mL), then CO₂ (10 or 56 atm) was added to the vessel at ambient temperature. The autoclave was heated up to the desired

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Table 1
Synthesis of ethylene carbonate^a.

entry	additive	base	T, °C	P, atm	t, h	conversion, %
1	–	Na ₂ CO ₃	110	56	2	75
2	–	NaOH	110	56	2	44
3	–	KOH	110	56	2	70
4	N(Bu) ₄ Br	Na ₂ CO ₃	110	56	2	92
5	N(Bu) ₄ I	Na ₂ CO ₃	110	56	2	91
6	N(Bu) ₄ Cl	Na ₂ CO ₃	110	56	2	92
7	N(Et) ₄ Cl	Na ₂ CO ₃	110	56	2	92
8	– ^b	–	110	56	2	0
9	N(Bu) ₄ Br ^c	–	110	56	2	0
10	N(Bu) ₄ Br	Na ₂ CO ₃	110	10	2	100
11	N(Bu) ₄ Br	K ₂ CO ₃	110	10	2	100
12	N(Bu) ₄ Br	K ₂ CO ₃	50	10	18	81
13	–	K ₂ CO ₃	50	10	18	79
14	N(Bu) ₄ Br	Na ₂ CO ₃	50	10	18	12
15	–	Na ₂ CO ₃	50	10	18	10
16	–	Na ₂ CO ₃	80	10	5	33
17	N(Bu) ₄ Br	Na ₂ CO ₃	80	10	5	40
18	–	K ₂ CO ₃	80	10	5	100 ^d
19	N(Bu) ₄ Br	K ₂ CO ₃	80	10	5	100

^a Catalyst - Acros® Silica gel for chromatography, 0.06–0.2 mm, 60 Å (25 mg), additive 5 mg, substrate (0.4 mL)\base = 1\1.1 mol.

^b Only silica gel (25 mg) was added.

^c Only N(Bu)₄Br (5 mg) was added.

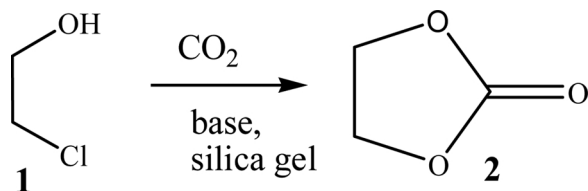
^d 93 % yield, extracted by MeOH.

temperature (5 min). The reaction proceeded at 110, 80 or 50 °C for necessary time. The reactor was cooled to room temperature in a water bath and the CO₂ pressure was released. The reaction products were analyzed by NMR after extraction by CDCl₃ (1.5 mL). Spectral characteristics of **2** are in accordance with literature data [15].

3. Results and discussion

The cyclization of 2-chloroethanol (**1**) with CO₂ (56 atm) into ethylene carbonate (**2**) was first tested using silica gel as a catalyst and Na₂CO₃ as a base (Scheme 1).

At 110 °C, the conversion to the desired carbonate **2** was 75 % (Table 1, entry 1). The use of KOH or NaOH as a base proved to be less effective (Table 1, entries 2 and 3). Moreover, the addition of 2-chloroethanol to KOH immediately causes an intensive evolution of ethylene oxide, which makes the process enough dangerous [17]. In contrast, the loading of 2-chloroethanol to inorganic carbonates is absolutely safe. Addition of tetrabutylammonium bromide which practically always is used as a co-catalyst in the reaction of CO₂ to form organic carbonates [14,18,19], resulted in an increase in the catalyst activity (Table 1, entry 4). In this case conversion reached 92 %. We also checked efficiency of other phase-transfer agents, such as N(Bu)₄I, N(Bu)₄Cl and N(Et)₄Cl, with the result that the same conversion was observed (Table 1, entries 5–7). It should be noted that the reaction with silica gel or tetrabutylammonium bromide without Na₂CO₃ did not proceed at all (Table 1, entries 8,9). We also checked the reaction without addition of CO₂ but no product was formed. Only 2-chloroethanol was detected in



Scheme 1. Synthesis of ethylene carbonate from 2-chloroethanol.

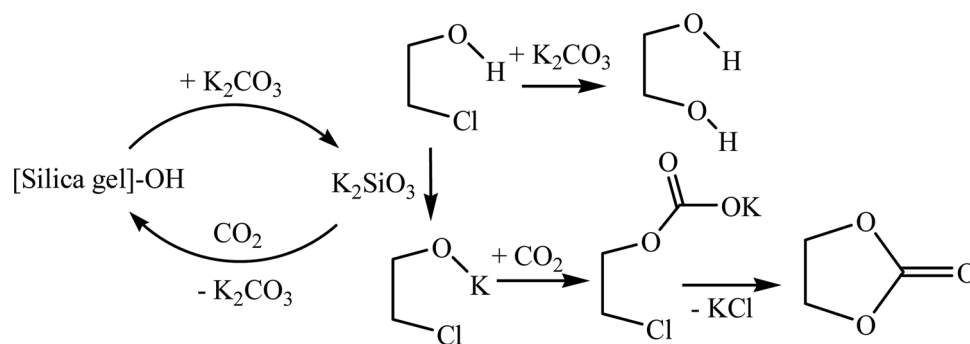
the reaction mixture according to ¹H NMR. Bearing in mind the possible formation of oxirane (bp 10.4 °C) in the reaction we have refrigerated the evolved gases by liquid nitrogen, but no liquid oxirane phase was observed. We noticed formation of a very small amount of a solid product which immediately turned gaseous after thawing without transformation into the intermediate liquid phase, which is typical for dry ice. A ¹H NMR spectra of the condensed phase (5 °C) dissolved in CDCl₃ showed no signals of organic compounds; only traces of water were detected. We also checked the above reaction using K₂CO₃ as a base and N(Bu)₄Br as an additive without adding silica gel. In this case 94 % conversion of 2-chloroethanol was obtained, but 41 % of ethylene glycol was formed in addition to the desired ethylene carbonate. This fact may be attributed to uncontrolled hydrolysis of 2-chloroethanol to ethylene glycol under alkaline conditions of the rather hygroscopic K₂CO₃. The use of silica gel solves the problem with the hygroscopic properties of the base due to a higher reaction rate. As reported earlier, the process is expected to proceed as shown in Scheme 2 but with a few exceptions [16]. Since the reaction of 2-chloroethanol with K₂CO₃ is unlikely to proceed and no CO₂ evolved as the reaction product, we suppose that K₂CO₃ can reversibly interact with acidic Si–OH groups of silica gel to form a highly alkaline potassium silicate which can promote the process. It was shown recently that inorganic silicates have the capacity to absorb CO₂ to form carbonates between room temperature and 130 °C, and recoverability of silica gel is the key factor of catalytic process [20,21].

From the practical perspective of the reaction process, the effect of CO₂ pressure was investigated. Surprisingly, upon decreasing the CO₂ pressure from 56 to 10 atm, a noticeable increase in reactivity was registered (Table 1, entry 10). The use of K₂CO₃ as a base also showed complete conversion (Table 1, entry 11) when the same reaction condition was tested. Probably, the increased solubility of 2-chloroethanol in the bulk of hot liquid CO₂ (near-critical conditions) with liquid-liquid phase behavior reduces the reaction rate [22].

To evaluate effect of temperature on conversion using K₂CO₃ and Na₂CO₃ as bases, we studied the process at a lower (50 °C) reaction temperature but the same CO₂ pressure (10 atm) and prolonged time. In this case, we obtained the product **2** with a good conversion using K₂CO₃, while Na₂CO₃ showed a significantly lower reaction rate (Table 1, entries 12–15). It should be noted that N(Bu)₄Br actually exerted no effect on conversion at this temperature. The reaction of 2-chloroethanol with CO₂ at a higher reaction temperature (80 °C) showed again that Na₂CO₃ gave a lower conversion to **2** compared to the more basic K₂CO₃ (Table 1, entries 16–19). Finally, it should be stressed that K₂CO₃ alone gives complete conversion of 2-chloroethanol to desired ethylene carbonate without any assistance from N(Bu)₄Br, the latter can only contaminate the product. So, the process requires the use of easily available 2-chloroethanol, inexpensive K₂CO₃, CO₂ at a sufficiently low pressure (10 atm), a moderate temperature (80 °C), a pinch of silica gel for column chromatography as a catalyst and lasts for reasonable time (5 h).

4. Conclusions

In summary, a “green”, simple, technically and economically feasible synthesis of valuable ethylene carbonate under mild reaction conditions was developed from 2-chloroethanol and CO₂ using K₂CO₃ as a base and silica gel as a catalyst. Moreover, reuse of insoluble silica gel and possible utilization of the reaction potassium waste as mineral fertilizer make the process very ecologically and technology promising [16,23]. Testing the industrial application of the process is in progress.



Scheme 2. Formation of ethylene carbonate from 2-chloroethanol.

Author contributions

Sergey E. Lyubimov: Wrote the paper.
 Anastasia A. Zvinchuk: Collected the data.
 Marina V. Sokolovskaya: Collected the data.
 Vadim A. Davankov: Other contribution.
 Biswajit Chowdhury: Contributed data or analysis tools.
 Pavel V. Zhemchugov: Collected the data.
 Ashot V. Arzumanyan: Performed the analysis.
 Aziz M. Muzafarov: Other contribution.

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