ISSN 0965-5441, Petroleum Chemistry, 2019, Vol. 59, No. 1, pp. 78–84. © Pleiades Publishing, Ltd., 2019.
Russian Text © G.Yu. Taranenko, G.V. Rybina, S.S. Srednev, A.E. Meshechkina, A.V. Tarasov, 2019, published in Neftekhimiya, 2019, Vol. 59, No. 1, pp. 76–82.

Catalyst Systems Based on a Metal Halide and a Quaternary Ammonium Salt in the 1,2-Epoxycyclopentane Carboxylation Reaction

G. Yu. Taranenko[a], G. V. Rybina[a, *], S. S. Srednev[a], A. E. Meshechkina[a], and A. V. Tarasov[a]

[a] *Yaroslavl State Technical University, Yaroslavl, Russia*

**e-mail: rybinagv@ystu.ru*

Received January 18, 2018; Revised March 18, 2018; Accepted July 26, 2018

Abstract—Results of a study of 1,2-epoxycyclopentane carboxylation to cyclopentene carbonate (CPC) in the presence of various catalyst systems have been described. It has been found that the reaction occurs most efficiently in the presence of cobalt (nickel) chloride (bromide) hydrate and a quaternary ammonium salt (TEAB, TBAB). It has been recommended that CPC should be synthesized under a CO_2 pressure of no less than 3.5 MPa at a temperature of 140–150°C without any solvent or in the medium of a solvent, such as target CPC, DMF, or *N*-MP, at a 1,2-epoxycyclopentane weight fraction in the feed mixture of no less than 25%. These conditions provide the formation of CPC with a selectivity of 97–99% and almost complete epoxide conversion within 2–4 h. It has been shown that the developed catalyst system can be recycled.

Keywords: carboxylation, 1,2-epoxycyclopentane, catalytic systems

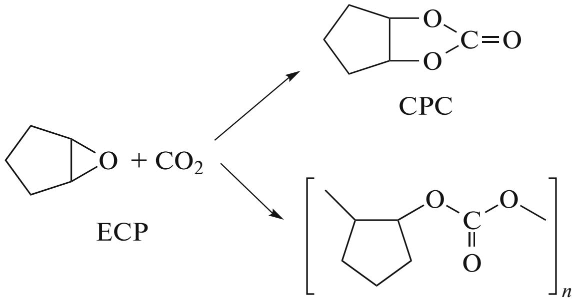
DOI: 10.1134/S096554411810016X

Cyclic organic carbonates (COCs) are promising products of industrial organic synthesis. Despite the wide ranges of practical application of these materials, low-molecular-weight COCs, such as ethylene carbonate and propylene carbonate, are being most commonly produced [1].

In recent decades, the attention of researchers has been increasingly given to the synthesis of alicyclic COCs, in particular, cyclopentene carbonate (CPC). The growing interest in CPC is attributed to the possibility of using this material both as a high-efficiency chlorine-free solvent [2] and as a monomer in the synthesis of a number of highly durable biodegradable urethane-containing polymers synthesized by an environmentally friendly isocyanate-free technology [3].

The currently available methods for synthesizing CPC from cyclopentene [4] and 1,2-cyclopentanediol [5, 6] have significant disadvantages, namely, the toxicity of the reactants used, a low CPC yield, and the formation of a significant amount of byproducts. Therefore, the production of CPC by the carboxylation of 1,2-epoxycyclopentane (ECP) can be thought of as the most promising, competitive, and environmentally friendly method (so-called "green chemistry" technology) for CPC synthesis.

The ECP carboxylation reaction can occur mostly via two routes:



poly(cyclopentene carbonate)

The route—the formation of CPC or poly(cyclopentene carbonate)—is largely determined by the nature of the catalyst.

A number of authors described the reaction between ECP with CO_2 in the presence of tetraethylammonium bromide (TEAB), tetramethylammonium bromide (TMAB), and tetrabutylammonium bromide (TBAB) quaternary ammonium salts (QASs) [7, 8] and a binary catalyst system composed of TEAB and an alkali metal bromide (iodide) [9]. Despite the high CPC yield, which achieves 92%, the catalyst looses activity because it undergoes partial decomposition under the reaction conditions.

A number of zinc-based organometallic catalysts for ECP carboxylation were proposed [4, 6, 10]; the use of these catalysts leads to the formation of poly(cyclopentene carbonate) with a yield of 65–99%.

At 25–70°C and a CO_2 pressure of 0.1–5.0 MPa, the EDS conversion does not achieve a value of more than 48% within 12–24 h. The cyclopentene oxide conversion of up to 56% was obtained under the same conditions within 3–6 h in the presence of binary salen catalysts (salen)CoCl/$PPNN_3$ and (salen)CrCl/TBAH; however, in this case, the CPC yield was 68–83% [10].

The use of porphyrin complexes of Mg, Co, Ni, Cu, Zn, and Al with a cocatalyst (QAS) [11] or a bifunctional 5,10,15,20-(porphyrin)AlCl/*N*-methylimidazole catalyst [12, 13] provides the formation of CPC with a yield of 54–90%. The reaction occurs at a temperature of 90–120°C and a pressure of 1–4.8 MPa in a medium of an aprotic solvent (HMPA, DMF) or the target CPC.

Thus, the reaction between ECP and carbon dioxide in the presence of most of the known catalysts occurs with a low CPC yield or a low ECP conversion; it is characterized by a long synthesis time, the need for using a solvent, the complexity of catalyst synthesis, and/or the impossibility of regenerating the catalyst.

The aim of this study is to develop effective catalyst systems for cyclopentene carbonate synthesis from 1,2-epoxycyclopentane and CO_2 and test the resulting catalysts.

EXPERIMENTAL

The ECP carboxylation reaction was run in a 60-cm^3 titanium reactor equipped with a jacket for circulating a heat transfer fluid (glycerol). A pressure gage, a sampling valve, and a CO_2 supply valve were embedded in the reactor cover; a well for a thermocouple was mounted into the reactor floor. Feed ECP, a solvent (20 cm^3), and the catalyst components were loaded into the carbon dioxide-purged reactor at room temperature. A constant CO_2 pressure was maintained by means of a reducing valve mounted on the line of gas supply from a cylinder. A required temperature was maintained by means of a thermostat with an accuracy of ± 1.0°C. Upon the achievement of an operating temperature in the reactor, a mechanical shaker was turned-on to provide a stirring speed of no less than 140 rpm. At regular intervals during the test, samples for analysis were taken from the reactor and placed into sealed tubes. The reaction time was counted from the time at which the shaker was turned-on.

Reaction products were analyzed on a Chromatec Kristall 5000.2 gas chromatograph equipped with a flame ionization detector and a CR-WAXms capillary column (30 m × 0.32 mm), using column temperature programming from 60 to 160°C at a heating rate of 10°C/min and the carrier gas (hydrogen) at a flow rate of 40 cm^3/min. The injected sample volume was 0.2 μL. Undecanol-1 was used as the internal standard.

The solvents DMF, DMAA, *N*-MP, acetonitrile, and formamide were of the "chemically pure" grade and were subjected to fractional distillation before synthesis; the assay was no less than 99.0% according to GLC data.

1,2-Epoxycyclopentane was produced by cyclopentene oxidation with an aqueous solution of hydrogen peroxide according to a known procedure [14] and isolated by distillation with a weight fraction of 99.5%; the residual water content was no more than 0.3%; $T_b = 102$°C; and $n_d^{20} = 1.4336$.

Gaseous carbon dioxide corresponded to GOST 8050-85.

Tetramethylammonium bromide (chemically pure) corresponded to TU 71-91-0; assay, 99.0%.

Other materials used were as follows: $CoCl_2 \cdot 6H_2O$ (GOST 4525-77), $AlCl_3 \cdot 6H_2O$ (GOST 3759-75), $CrCl_3 \cdot 6H_2O$ (GOST 4473-78), $SnCl_2 \cdot 2H_2O$ (GOST 36-78) and $NiCl_2 \cdot 6H_2O$ (GOST 4038-79), all of the chemically pure grade, and reagent grade KI (GOST 4232-74).

Cyclopentene carbonate was isolated by rectification with a weight fraction of 99.7%, $T_b = 170$°C/2 mmHg, and $T_m = 32.5$–35°C.

The CPC structure was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer using DMSO-d_6 as the solvent and tetramethylsilane as the internal standard.

Infrared spectra were recorded on a PerkinElmer Spectrum RX-1 FTIR spectrometer at wavelengths of 700–4000 cm^{-1}. The analyte had the form of a suspension in vaseline oil; KBr plates were used. Mass spectra were recorded on a Shimadzu Prominence LCMS-2020 high-performance liquid chromatograph–mass spectrometer equipped with a chromatographic column ($T = 40$°C; eluent, acetonitrile) and a mass spectrometer (LCMS-2020; m/z range, 0–2000; ionization modes, ESI/ACPI).

IR, ν/cm^{-1}: 1780 (C=O), 1172, 1112, 1047 (C–O–C). ^{1}H NMR (400 MHz, δ, ppm): 1.45–1.62 (m, 1H, H^5), 1.62–1.77 (m, 3H, H^5, H^4, H^6), 1.88–2.00 (m, 2H, H^4, H^6), 5.12–5.20 (m, 2H, H^{3a}, H^{6a}). ^{13}C NMR (75 MHz, δ, ppm): 21.38 (1C, C^5), 32.44 (2C, C^4, C^6), 81.89 (2C, C^{3a}, C^{6a}), 155.07 (1C, C=O). ESI, m/z (I_{rel} (%)): 127 $[M]^+$. It was found that, in the presence of the $CoCl_2 \cdot 6H_2O$–TEAB catalyst system, the *cis*-isomer of CPC is formed.

RESULTS AND DISCUSSION

A catalyst system composed of a cobalt (nickel) halide and DMF was proposed previously; it showed high efficiency for the synthesis of cyclic carbonates from monoalkyl-substituted C_5–C_{16} ethylene oxides,

C_4 and C_8 diene monoepoxides, epichlorohydrin, and styrene oxide [15]. Therefore, it was of interest to use this system in the ECP carboxylation reaction. To compare the activity, tests were conducted in the presence of TEAB and KI catalysts (Table 1), which are most commonly used in commercial syntheses of lower COCs [4]. The ECP carboxylation reaction was run in a DMF medium and in the solvent-free mode.

In the absence of a solvent, the formation of CPC occurs with a high selectivity of 89.5% only in the presence of the TEAB catalyst (Table 1, entry 5). Under the same conditions, KI and $CoCl_2 \cdot 6H_2O$ hardly catalyze the ECP conversion to CPC: the process selectivity is extremely low—2 or 3% at an epoxide conversion of 3 or 12%, respectively (Table 1, entries 3, 7). This finding is apparently attributed to the low solubility of metal halides in cyclopentene oxide.

It was found that DMF is capable of catalyzing the reaction between CO_2 and ECP. Within 3 h, the epoxide conversion achieves 5.5% at a CPC selectivity of 35% (Table 1, entry 1). The catalytic activity of DMF in the carboxylation of aliphatic epoxides was previously observed by Rui et al. [16].

It was shown that the efficiency of the catalysts increases if the reaction is run in a DMF medium. Thus, in the presence of TEAB, at a temperature of 150°C and a CO_2 pressure of 2 MPa, the ECP conversion achieved 90.1% for 3 h with a CPC selectivity of 91.3% (Table 1, entry 4). In the case of catalysis by cobalt chloride, the ECP conversion reached 87%; however, the selectivity remained low at a level of no more than 48% (Table 1, entry 2). The use of KI as a CPC synthesis catalyst is extremely inefficient even in a DMF medium (Table 1, entry 6).

Thus, the use of $CoCl_2 \cdot 6H_2O$ in a DMF medium for CPC synthesis from ECP and CO_2 did not provide the same high values as those obtained in the carboxylation of acyclic C_5–C_{16} epoxides [15]. This finding is apparently due to the fact that the reactivity of cycloolefin oxides in this reaction is lower than the reactivity of aliphatic epoxides, a difference that was noted in a number of papers [10, 17].

It is known that in the literature, binary catalyst systems are considered to be the most effective catalysts for the carboxylation of epoxides of various structures [4]. They include Lewis acid (metal halide) and a nucleophilic component (typically, a quaternary ammonium salt). Therefore, binary catalyst systems based on chromium, aluminum, cobalt, and nickel halides in combination with quaternary ammonium salts were tested in this study (Table 2). Organometallic catalysts based on these metals were proposed by a number of authors for the carboxylation of alicyclic C_6–C_{12} epoxides [16–18].

Analysis of the results (Table 2) showed that the highest activity in the targeted CPC synthesis is exhibited by the catalyst systems based on a cobalt (or nickel) halide and TEAB (or TBAB) both in a solvent medium (DMF, *N*-MP) and in the absence of a solvent (Table 2, entries 4–7, 12, 13). At a temperature of 150°C and a pressure of 2 MPa, this binary catalyst system provided an ECP conversion of more than 99% with a CPC selectivity of up to 97%. Data on the influence of the nature of the solvent on the carboxylation reaction parameters (Table 1; Table 2, entries 6–11) show that it has a significant effect on the cycloaddition reaction rate, as was repeatedly reported by other authors [10]. Apparently, the role of the solvent goes beyond changing the physicochemical properties of the reaction medium: it is part of the catalyst system.

Table 1. Effect of the solvent and the catalyst nature on the cyclopentene carbonate synthesis parameters. Conditions: temperature, 150°C; carbon dioxide pressure, 2 MPa; weight fraction of epoxycyclopentane in the feed mixture, 2.9 mol/dm^3; catalyst concentration, 0.0345 mol/mol ECP; and reaction time, 180 min

No.	Catalyst	Solvent	ECP conversion, %	CPC selectivity, %
1	None	DMF	5.55	35.11
2	$CoCl_2 \cdot 6H_2O$	DMF	86.03	48.07
3		None	12.53	2.33
4	TEAB	DMF	90.12	91.34
5		None	66.46	89.53
6	KI	DMF	22.55	8.71
7		None	3.14	3.35

According to expectations, in the case of using hydrates of metal salts in carboxylation, a secondary reaction is the ECP hydrolysis to form CPDiol (Table 2), which hinders the isolation of CPC from the reaction mixture. In addition, the CPC synthesis products included cyclopentanone, which is formed during the ECP isomerization in the presence of Lewis acids [19], and halohydrins, the formation of which was also observed in the divinyl oxide carboxylation [15]. Poly(cyclopentene carbonate) was not detected in the reaction mixture.

Studies of the effect of the initial ECP concentration on the parameters of CPC synthesis in the presence of the catalyst system composed of $CoCl_2 \cdot 6H_2O$ and TEAB in a DMF medium (Fig. 1) revealed that, with an increase in the ECP content in the feed mixture to 2 mol/dm^3, the epoxide conversion and the CPC selectivity rapidly increase; within 240 min, these parameters achieve 93.2 and 97.1%, respectively. A further increase in the initial ECP concentration leads only to a slow increase in the ECP conversion; at a C_0(ECP) value of 8.93 mol/dm^3 (solvent-free synthesis), the epoxide conversion was 98.3% with a CPC

Table 2. Effect of the nature of the metal halide and the solvent on the parameters of CPC synthesis in the presence of a binary catalyst system with TEAB. Conditions: temperature, 150°C; CO_2 pressure, 2.0 MPa; initial ECP concentration, 2.9 mol/dm^3; MeH catalyst concentration, 0.0041 mol/mol ECP; MeH : TEAB catalyst molar ratio, 1 : 4; and reaction time, 240 min

No.	Metal halide	Solvent	ECP conversion, %	Selectivity, %		
				CPC	CPDiol*	other
1	$AlCl_3 \cdot 6H_2O$	DMF	73.78	22.55	14.10	63.35
2	$CrCl_3 \cdot 6H_2O$	DMF	96.36	87.18	12.80	0.02
3	$SnCl_2 \cdot 2H_2O$	DMF	96.41	83.29	16.45	0.26
4	$NiCl_2 \cdot 6H_2O$	DMF	97.16	96.88	2.77	0.35
5	$NiBr_2 \cdot 3H_2O$	DMF	98.80	96.28	2.43	1.29
6	$CoCl_2 \cdot 6H_2O$	DMF	99.71	97.15	2.81	0.04
7		*N*-MP	99.41	96.01	2.17	1.82
8		DMAA	87.54	96.26	0.72	1.57
9		Formamide	69.00	94.47	1.27	4.26
10		Acetonitrile	31.49	96.80	2.47	0.73
11		CPC	99.63	97.84	2.11	0.05
12		None**	98.30	98.11	0.81	1.08
13		DMF***	99.12	96.84	3.03	0.13

* 1,2-Cyclopentadiol. ** The initial ECP concentration is 8.93 mol/dm^3. ** TBAB QAS.

selectivity of 98.1%. Apparently, the resulting CPC contributes to the activation of the reaction between ECP and CO_2. This assumption is supported by high parameters of cyclocarbonate synthesis in the target CPC medium and in the absence of a solvent (Table 2, entries 11, 12). The further studies of the ECP carboxylation reaction were conducted in the absence of a solvent.

The effect of the concentration of the catalyst system components on the CPC synthesis parameters at a constant feed molar ratio of $CoCl_2 \cdot 6H_2O$: TEAB =

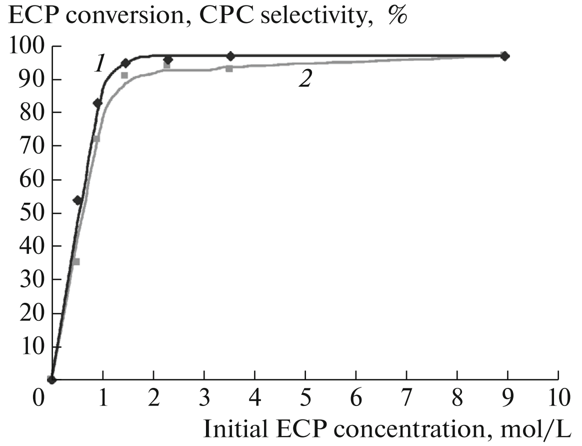


Fig. 1. Effect of the initial ECP concentration on (*1*) CPC selectivity (%) and (*2*) ECP conversion (%). Conditions: temperature, 150°C; CO_2 pressure, 2.0 MPa; molar ratio, $CoCl_2 \cdot 6H_2O$: TEAB = 1 : 1; $CoCl_2 \cdot 6H_2O$ concentration, 0.0345 mol/mol ECP; solvent, DMF; and reaction time, 240 min.

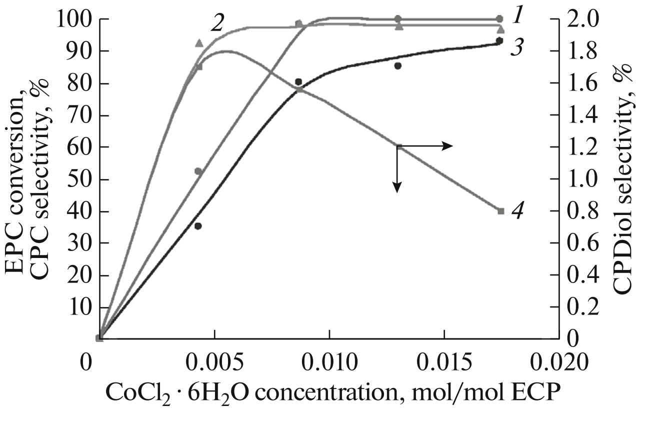


Fig. 2. Effect of the concentration of the catalytic system components on the ECP conversion and the CPC and CPDiol selectivity: ECP conversion (%) within (*1*) 240 and (*3*) 120 min, (*2*) CPC selectivity (%) within (line) 240 and (symbols) 120 min, and (*4*) CPDiol selectivity (%) within 240 min. Conditions: temperature, 150°C; CO_2 pressure, 2.0 MPa; initial ECP concentration, 8.93 mol/dm^3; molar ratio, $CoCl_2 \cdot 6H_2O$: TEAB = 1 : 1; solvent-free synthesis.

Table 3. Effect of the molar ratio of the $CoCl_2 \cdot 6H_2O$–TEAB catalyst system components on the CPC synthesis parameters. Conditions: temperature, 150°C; CO_2 pressure, 2.0 MPa; initial ECP concentration, 8.93 mol/dm^3; solvent-free synthesis

No.	$CoCl_2 \cdot 6H_2O$: TEAB molar ratio	Time, min	ECP conversion, %	Selectivity, %		
				CPC	CPDiol	other*
TEAB concentration of 0.0044 mol/mol ECP						
1	0.125 : 1	120	61.1	98.6	1.1	0.3
		180	74.8	98.0	1.2	0.8
		240	83.1	97.9	1.1	1.0
2	0.25 : 1	120	74.3	98.1	0.4	1.5
		180	90.9	97.8	0.4	1.8
		240	97.0	97.8	0.4	1.8
3	0.5 : 1	120	84.1	98.0	0.7	1.3
		180	96.0	97.5	0.7	1.8
		240	98.3	97.5	0.7	1.8
4	1 : 1	120	83.0	98.3	0.8	0.9
		180	97.3	98.5	0.7	0.8
		240	98.1	98.6	0.7	0.7
5	2 : 1	120	80.5	97.3	1.0	1.7
		180	93.1	96.2	1.0	2.8
		240	98.0	96.5	1.0	2.5
$CoCl_2 \cdot 6H_2O$ concentration of 0.0044 mol/mol ECP						
6	1 : 2	120	97.9	98.7	0.7	0.6
		180	99.3	98.8	0.7	0.5
		240	99.6	99.1	0.7	0.2
7	1 : 0.5	120	38.6	96.2	1.5	2.3
		180	52.0	96.3	1.5	2.2
		240	65.3	96.2	1.4	2.4

* Cyclopentanone and 2-chlorocyclopentanol-1.

1 : 1 was studied (Fig. 2). It was found that, with an increase in the $CoCl_2 \cdot 6H_2O$–TEAB catalyst system concentration from 0.0044 to 0.0087 mol/mol ECP, at a molar ratio of the components of 1/1, the ECP conversion and the CPC selectivity increase and achieve a maximum value of 98.5–99.2% within 240 min. With a further increase in the catalyst content in the reaction mixture to 0.0348 mol/mol ECP, these parameters of the process remain almost unchanged (curves *1, 2*); however, the CPDiol yield decreases (curve *4*) and the proportion of the epoxide isomerization products increases. It should be noted that the reaction time (240 or 120 min) affects only the epoxide conversion (curves *1, 3*); the CPC selectivity does not change over the entire duration of the reaction (curve *2*, line and symbols).

Assuming that the initial system components primarily form a catalytic complex (complexes) that activates the carboxylation reaction, we studied the effect of the molar ratio between $CoCl_2 \cdot 6H_2O$ and TEAB (Table 3). In this case, both the excess and deficiency of the catalyst system components with respect to each other were varied.

In the case of variation in the cobalt chloride content in the reaction mixture from 0.0006 to 0.0088 mol/mol ECP (Table 3, entries 1–5) at a constant TEAB concentration of 0.0044 mol/mol ECP, it is evident that the ECP conversion does not exceed 84% in the entire $CoCl_2 \cdot 6H_2O$ concentration range with a CPC selectivity of about 98% at a reaction time of 120 min. The ECP conversion of at least 97% can be achieved within 4 h at a $CoCl_2 \cdot 6H_2O$: TEAB molar

Table 4. Effect of CO_2 pressure and temperature on the ECP carboxylation reaction. Conditions: initial ECP concentration, 8.93 mol/dm^3; $CoCl_2$ concentration, 0.0010 mol/mol ECP; and $CoCl_2 \cdot 6H_2O$: TEAB molar ratio, 1 : 4

No.	Temperature, °C	CO_2 pressure, MPa	Time, min	ECP conversion, %	Selectivity, %		
					CPC	CPDiol	other
1	150	1.0	120	65.9	97.4	0.5	2.1
			180	81.5	97.1	0.5	2.4
			240	91.1	97.1	0.5	2.4
2	150	2.0	120	74.3	98.1	0.4	1.5
			180	90.9	97.8	0.4	1.8
			240	**97.0**	**97.8**	0.4	1.8
3	150	3.5	120	91.2	98.5	0.4	1.1
			180	**98.8**	**98.7**	0.4	0.9
			240	**99.9**	**98.0**	0.4	1.6
4	150	4.5	120	88.2	98.4	0.4	1.2
			180	**98.1**	**98.6**	0.4	1.0
			240	**99.5**	**98.4**	0.4	1.2
5	110	2.0	240	2.4	90.9	2.5	6.6
6	130	2.0	240	15.7	96.4	2.3	1.3
7	160	2.0	120	52.5	95.7	2.0	2.3*
			180	77.6	95.5	1.9	2.6*
			240	89.4	95.7	1.8	2.5*

* Mostly high-boiling compounds.

ratio of 0.25–0.5 : 1 (Table 3, entries 2, 3) or within 3 h at a ratio of 1 : 1 (Table 3, entry 4). In this case, the formation of CPC occurs with a selectivity of 97.5–98%. However, even at a cobalt chloride concentration of 0.0088 mol/mol ECP (Table 3, entry 5), the CPC selectivity decreases to 96% with increasing reaction time. With an increase in the $CoCl_2 \cdot 6H_2O$ concentration, the CPDiol yield on a converted ECP basis slightly increases and achieves 0.8 ± 0.2%. This fact is apparently attributed to the introduction of a larger amount of crystallization water with the catalyst. At the same time, the yield of other byproducts, mostly cyclopentanone, exhibits a minimum at an equimolar ratio of cobalt chloride and TEAB (Table 3, entry 4). It should be noted that the selectivity for CPDiol and other byproducts varies only slightly with an increase in the reaction time from 1 to 3 h.

A moderate TEAB content in the reaction mixture (0.0022 mol/mol ECP)—two times lower than the cobalt chloride hexahydrate content (Table 3, entry 7)—leads to a significant decrease in the carboxylation rate, although the CPC selectivity remains fairly high (96%). An increase in the TEAB content to 0.0044 mol/mol ECP and higher values provides an increase in the reaction rate. Owing to this effect, the ECP conversion achieved a value above 99% within 3 h of reaction at a CPC selectivity of about 99% (Table 3, entry 6). It should be noted that the molar excess of $CoCl_2 \cdot 6H_2O$ with respect to TEAB leads to an increase in the proportion of ECP isomerization products in the reaction mixture (Table 3, entries 5, 7).

In addition, the data of Tables 2 and 3 suggest that in order to achieve high parameters in the CPC synthesis, it is important to maintain not only a certain molar ratio of the components of the binary system, but also their total content relative to the initial ECP concentration.

The effect of the carbon dioxide pressure and the reaction temperature was examined; it was found that they significantly affect only the ECP conversion (Table 4).

It was found that an almost complete consumption of the epoxide can be achieved at a CO_2 pressure of 3.5 MPa and above within 4 h. In this case, the CPC selectivity is no less than 98% (Table 4, entries 3, 4). With an increase in pressure, the CPDiol yield remains almost unchanged at a level of 0.4–0.5%, while the formation of other byproducts decreases to 1 ± 0.2% at a pressure of 4.5 MPa. At temperatures of 110 and 130°C (Table 4, entries 5, 6), the reaction rate is extremely low; at 130°C, the ECP conversion does not exceed 20% within 240 min. The decrease in the process rate at 160°C (entry 7) is apparently due to the partial thermal degradation of TEAB [20]. The CPDiol content in the reaction mixture increases; the formation of other high-boiling compounds is observed (Table 4, entry 7).

Thus, the studies of the CPC synthesis by ECP carboxylation have made it possible to select a catalyst system composed of available components, namely, cobalt (nickel) chloride (bromide) hydrate and a quaternary ammonium salt (TEAB, TBAB). It is recommended that the CPC synthesis should be conducted under a carbon dioxide pressure of 3.5–4.5 MPa at a temperature of 140–150°C without a solvent or in a solvent medium. Cyclopentene carbonate, DMF, or *N*-MP can be used as the solvent at a weight fraction of ECP in the feed mixture of no less than 25%. When loading the reaction mixture components, it is necessary to provide a $CoCl_2$ concentration of 0.0043–0.0357 mol/mol ECP at a $CoCl_2 \cdot 6H_2O$: TEAB molar ratio of 1 : 4 to 1 : 1. These conditions ensure the formation of CPC with a selectivity of 97–99% at almost complete epoxide conversion within 2–4 h.

Using the above-specified synthesis parameters, a set of large-scale CPC synthesis runs was conducted in the presence of the $CoCl_2 \cdot 6H_2O$–TEAB catalyst system in a DMF medium and in the absence of a solvent. In the case of using a 1-dm^3 reactor, the ECP conversion and the CPC selectivity achieved 99.1–99.6% and 97.5–99%, respectively, within 240 min. Cyclopentene carbonate was isolated from the reaction mixture by vacuum distillation and then washed with water at 80°C to remove impurities. The raw CPC was dried in a vacuum at 20 mmHg and 20°C. The content of the basic substance of CPC was no less than 99.5%.

The bottom residue after the distillation of the products, which has the form of a catalyst solution in CPC with a cobalt content of 4.39%, can be recycled. It has been shown that it can be repeatedly used as a reaction catalyst in four cycles without any decrease in the CPC synthesis parameters.

REFERENCES

1. T. Sakakura and K. Kohno, Chem. Commun., No. 11, 1312. 2009.
2. M. Aresta, A. Dibenedetto, and E. Quaranta, *Reaction Mechanisms in Carbon Dioxide Conversion* (Springer, Berlin, 2016).
3. V. V. Mikheev, *Nonisocyanate Polyurethanes* (KNITU, Kazan, 2011) [in Russian].
4. M. Carmen, F. Giulia, W. Arjan, and J. Kleij, ACS Catal. **5**, 1353 (2015).
5. I. Taisuke, I. Takehiko, N. Itaru, and O. Masashi, Chem. Pharm. Bull. **50**, 83 (2002).
6. G. Bartolo, M. Raffaella, S. Giuseppe, et al., ChemSusChem **4**, 1778 (2011).
7. J. F. Cooper and M. Lichtenwalter, US Patent No. 2773070 (1956).
8. G. W. Crosby and A. F. Millikan, US Patent No. 2994705 (1961).
9. H. Okamoto and K. Someya, US Patent No. 7199253.
10. D. J. Darensbourg, W. C. Chung, and S. J. Wilson, ACS Catal, **3**, 3050 (2013).
11. *Transformation and Utilization of Carbon Dioxide,* Ed. by B. M. Bhanage and M. Arai (Springer, Berlin, 2014).
12. M. J. Cannarsa, H.-N. Sun, and H. S. Kesling, Jr., EP Patent No. 0321207 (1989).
13. J. William and J. Kruper, US Patent No. 4663467 (1987).
14. L. V. Mel'nik, A. E. Meshechkina, G. V. Rybina, et al., Pet. Chem. **52**, 313 (2012).
15. G. V. Rybina, L. I. Bobyleva, and S. S. Srednev, Russ. J. Appl. Chem. **76**, 842 (2003).
16. L. Rui, T. Xin, L. Xiaofang, and H. Changwen, Pure Appl. Chem. **84**, 621 (2012).
17. D. J. Darensbourg and W. Matthew, Coord. Chem. Rev. **153**, 155 (1996).
18. G. Richard, R. C. Austin, and R. M. Michaelson, US Patent No. 4824969 (1989).
19. G. V. Rybina, L. V. Mel'nik, S. S. Srednev, et al., RU Patent No. 2448945 (2012).
20. E. V. Dehmlow and S. S. Dehmlow, *Phase Transfer Catalysis*, 2nd Ed. (Chemie, Weinheim, 1983).

Translated by M. Timoshinina