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Cyclic Carbonates from Carbon Dioxide and Oxiranes

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The synthesis of cyclic carbonates **2** by reaction of carbon dioxide with oxiranes **1** in the presence of alkali metal salt-phase-transfer agent catalysts is reported. A reaction mechanism is proposed.

(Keywords: Crown ether; Phasetransfer catalyst)

Synthesen cyclischer Carbonate aus CO_2 *und Oxiranen*

Synthesen cyclischer Carbonate **2** durch Umsetzung von CO_2 mit Oxiranen **1** in Gegenwart von Alkalimetall-Phasentransfer-Katalysatoren werden beschrieben. Ein möglicher Reaktionsmechanismus wird vorgeschlagen.

Introduction

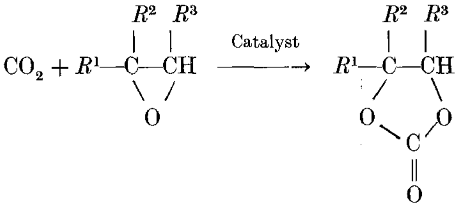
The chemistry of carbon dioxide has received much attention in recent years. It has been considered as a monomer in polymerization and polycondensation reactions, which have been reviewed elsewhere[1]. Attention has also been paid to its reaction with epoxides leading to cyclic alkylene carbonates. From these carbonates polymeres having ester[2] as well as carbonate and ether[3] linkages were synthesized.

The literature reports[4, 5] on the synthesis of alkylene carbonates by the CO_2 reactions with oxiranes in the presence of various catalysts, such as quaternary ammonium and alkali metal salts or some other metal derivatives. These reactions, however, do not proceed under mild conditions in high yields and, when catalyzed by transition metal complexes, they were accompanied in some cases by oxirane homopolymerization[6]. However, in the case of the nickel(O) phosphine complexes they produced cyclic carbonates in rather high yields[5].

Although alkali metal salts appeared to be rather poorly active catalysts for the CO_2-expoxide reaction, the introduction of a crown ether or another phase-transfer agent to the system could be expected to enhance their catalytic activity. This could cause the activation of the respective anion to such an extent that the cyclic alkylene carbonate was produced in a high yield under mild conditions. We succeded recently in convenient syntheses of linear carbonate monomers by reactions of CO_2 with alkali metal alkoxide and α,ω-dihalocompounds[7], as well as alkali metal carbonate with alkyl halides[8], promoted by anion activating agents. In the present work an attempt has been made to react carbon dioxide under mild conditions with epoxide compounds in the presence of catalytic systems composed of the alkali metal salt and the anion activating agent.

Results

By selecting the conditions and catalysts, the CO_2 reaction with epoxides **1** (Tables 1–5) proceeds according to Eq. (1). The structures of the products (a cyclic carbonate **2**) was confirmed by elemental analysis as well as by IR and ^{1}H-NMR spectroscopy.



(1)

1, 2	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	H	—$(CH_2)_4$—	
d	C_6H_5	H	H
e	CH_2Cl	H	H
f	CH_2Cl	CH_3	H

1, 2	R^1	R^2	R^3
g	CH_2Br	H	H
h	CH_2OH	H	H
i	$CH_2OC_4H_9$	H	H
j	$CH_2OCH_2CHCH_2$	H	H
k	$CH_2OC_6H_5$	H	H

The effect of the catalyst on the yield of 4-chloromethyldioxolone-2 (**2e**) formed from the reaction of CO_2 with epichlorohydrin (**1e**) was investigated.

Table 1 shows that the above reaction proceeds in the presence of alkali metal halides and carbonates with relatively low yields (up to ca. 30%). The use of a crown ether for the alkali metal causes a remarkable

Table 1. *Yield of 4-chloromethyldioxolone-2* **2 e** *in the reaction of* CO_2 *with epichlorohydrin* **1 e** *in the presence of alkali metal salt—crown ether catalytic systems*[a]

Catalyst system	Yield of **2 e**[b] %
Na_2CO_3—15-crown-5	95
K_2CO_3	7
K_2CO_3—18-crown-6	98
LiCl	24
NaCl	26
KCl	32
LiCl—15-crown-5	36
NaCl—15-crown-5	89
KCl—18-crown-6	93
KI	29
KI—18-crown-6	97
CH_3COOK—18-crown-6	83
L-(+)-KOOC[CH(OH)]$_2$COOK—18-crown-6	84
C_6H_5OK—18-crown-6	82

[a] Reaction conditions: **1 e**, 0.18 mol, CO_2 initial pressure 40 atm; alkali metal salt, 1.2 mmol, crown ether, 0.38 mmol; temp. 120 °C, time 24 h.

[b] Calculations based on **1 e**.

increase in the yield of **2 e**, which in some cases, e.g. in the presence of potassium carbonate or iodide and 18-crown-6 ether reaches almost 100%. The reaction of CO_2 with **1 e** proceeds also with high yield in systems containing crown ether and other alkali metal salts as catalysts such as potassium carboxylates and phenolates.

The reactions of CO_2 with oxiranes without halomethyl substituents at the ring in the presence of the alkali metal carbonate—crown ether catalyst proceeds with very low yields of **2** (1–2%). Also in the presence of alkali metal carboxylates activated by a crown ether these reactions did not proceed. On the other hand, when alkali metal bicarbonate or phenolates with a crown ether as catalyst were applied, the reaction of CO_2 with an oxirane without a halomethyl substituent at the ring gave **2**. However, the yield of **2** in these reactions was much lower than in the analogous reaction of CO_2 with epihalohydrin. These results are illustrated by the reaction of several oxiranes **1 b**, **d**, **k**, given in Table 2. Taking into account the higher activity of the potassium carbonate—crown ether catalyst in the reaction of CO_2 with epihalohydrin than with the other epoxy compounds studied, an analysis of the catalyst remaining in the mixture was carried out:

Table 2. *Yield of cyclic carbonate* **2** *in the reaction of* CO_2 *with the epoxide* **1** *in the presence of the potassium salt—18-crown-6 ether catalytic systems*[a]

Epoxide compound **1**	Potassium salt	Reaction temp. °C	Yield of **2**[b] %
1b	K_2CO_3	120	2
	$KHCO_3$	120	7
	$KOOC(CH_2)_8COOK$[c]	80	traces
	C_6H_5OK	120	12
	$2,4\text{-}(NO_2)_2C_6H_3OK$	120	5
1d	K_2CO_3	120	1
1e	K_2CO_3	70	32
		80	68[d]
		100	91[d]
		120	98
		130	92
1g	K_2CO_3	80	96
1k	K_2CO_3	120	1

[a] Reaction conditions: **1**, 0.18 mol, CO_2 initial pressure 40 atm, potassium salt, 1.4 mmol, 18-crown-6, 0.38 mmol, time 24 h.

[b] Calculations based on **1**.

[c] **1b**, 0.25 mol, potassium salt, 0.8 mmol, 18-crown-6, 0.19 mmol.

[d] Alkali metal salt, 1.2 mmol.

Table 3. *Effect of the structure of epoxide* **1** *on the yield of the cyclic carbonate* **2** *in the reaction of* CO_2 *with* **1** *in the presence of the KI—18-crown-6 ether catalytic system*[a]

Epoxide compound **1**	**a**	**b**	**b**[c]	**c**	**d**	**e**	**f**[d]	**g**	**h**	**i**	**j**	**k**
Yield of **2**[b] %	91	90	95	25	68	97	92	96	73	90	90	75

[a] Reaction conditions: **1**, 0.18 mol, CO_2 initial pressure 40 atm, KI, 1.2 mmol, 18-crown-6, 0.38 mmol, temp. 120 °C, time 4 h.

[b] Calculations based on **1**.

[c] Temp. 100 °C, time 24 h.

[d] **1**, 0.1 mol, temp. 90 °C, time 24 h.

In the reaction with epihalohydrin **1e** a large amount of KCl (with respect to K_2CO_3) was found. It follows that K_2CO_3 activated by the crown ether reacts with **1e** giving KCl, which in a finely dispersed state with the crown ether is a very active catalyst for the reaction of CO_2 with **1e**. The reaction of CO_2 with **1e** in the presence of $L(+)$ tartaric acid and crown ether as catalyst yields optically inactive **2e**. This confirms the mechanism, in which the reaction is catalyzed by the *in situ* formed KCl being of course optically inactive.

Table 4. *Relationship between the kind of the phase-transfer agent and the yield of 4-chloromethyldioxolone-2* **2e** *in the reaction of* CO_2 *with epichlorohydrin* **1e** *in the presence of KI—phase-transfer agent catalytic systems*[a]

Phase-transfer agent			**2e**	
	Amount		Amount	Yield[b]
	g	mmol	g	%
18-crown-6	0.1	0.38	24.2	97
DB-18-crown-6	0.1	0.27	23.2	93
15-crown-5	0.1	0.45	24.2	97
DABCO	0.1	0.9	23.7	95
TMEDA	0.2	1.7	23.0	92
Polyglyme 300	0.75	2.5	8.3	33
Polyglyme 600	0.75	1.24	15.5	62
Poly(ethylene glycol) 1500	1.0	0.67	11.2	45
TEBA	0.2	0.88	22.7	91

[a] Reaction conditions: **1e**, 16.6 g, 0.18 mmol, CO_2 initial pressure 40 atm, KI, 0.2 g, 1.2 mmol, temp. 120 °C, time 24 h.

[b] Calculations based on **1e**.

Table 3 presents the yields of cyclic carbonates **2a–k** in the reactions of CO_2 with epoxy compounds in the presence of the catalytic system KI—18-crown-6 at 120 °C within 4 h. The highest yields of **2** were obtained in the reaction with **1e–g**. High yields of **2** (ca. 90%) were also obtained in the reaction of CO_2 with *n*-butyl- and allylglycide ethers (**1i, j**) as well as with ethylene and propylene oxides (**1a, b**). Phenyl derivatives, e.g. styrene oxide (**1d**) and phenylglycide ether (**1k**) gave **2** in ca. 70% yield, but the 2,3-disubstituted cyclohexene oxide **1c** gave the cyclic carbonate in low yields (of only 25%).

From these studies (Table 2) it appears that the reaction of CO_2 with the epoxy compound proceeds with the highest yields of **2** at 120 °C. A decrease of the reaction temperature causes a considerable decrease in the yields of the cyclic carbonate. Above 120 °C, however, the yield of **2** decreases somewhat resulting from side reactions (opening of the dioxolon ring in **2** by the catalyst[9]). In the reactions both of epihalohydrins as well as of other epoxides at various temperatures no oxirane homopolymers or CO_2-oxirane copolymers were found. Due to the lack of side products in the reactions of CO_2 with epoxides, the catalyst recovered by distilling **2** from the reaction mixture could be reused.

The yield of **2** depended to a great extent on the agent activating the catalyst. Instead of the crown ether, also other phase-transfer agents, such as 1,4-diazabicyclo-[2,2,2]-octane (*DABCO*), *N,N,N,N*-tetramethylethylenediamine (*TMEDA*) and also triethylbenzylammonium chloride (*TEBA*) could be used for the CO_2/epoxide reaction and give rise to a high conversion of CO_2 and the oxirane to the cyclic carbonate.

Table 5. *Relationship between the CO_2 pressure and yield of 4-chloromethyldioxolone-2* **2e** *in the reaction of CO_2 with epichlorohydrin* **1e** *in the presence of the KI—18-crown-6 ether catalytic system*[a]

CO_2 initial pressure atm	1[b,c]	6[c]	7	16	30	40
Yield of **2e**[d] %	8	76	54	85	91.5	97

[a] Reaction conditions: **1e**, 0.18 mol, mole ratio CO_2/**1e** = 1.5, KI, 1.2 mmol, 18-crown-6, 0.38 mmol, temp. 120 °C, time 24 h.

[b] Constant pressure during the reaction.

[c] Temp. 116 °C.

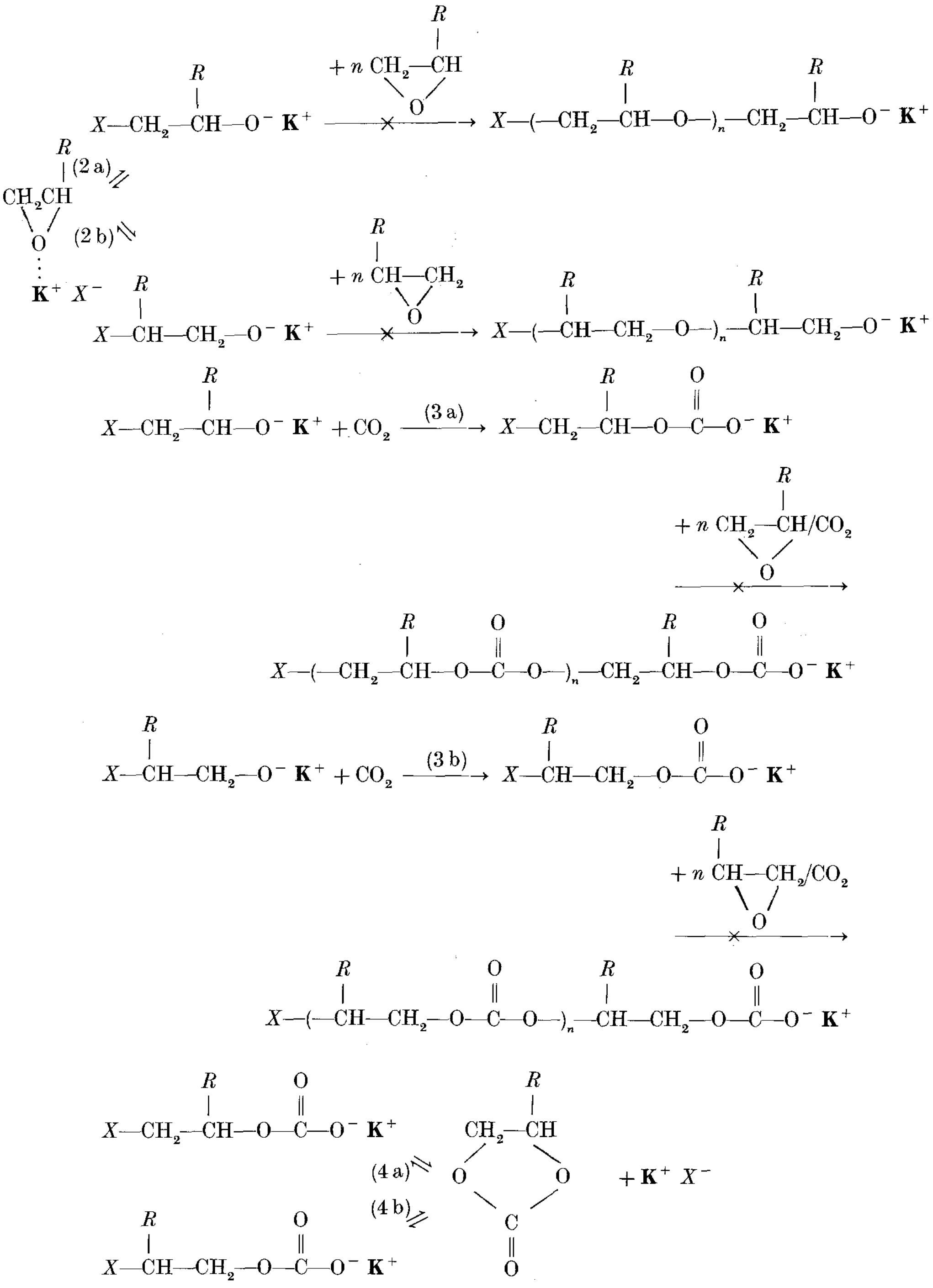
[d] Calculations based on **1e**.

For example, in the case of **2e** the conversion was higher than 90% (Table 4). Polyglymes and poly(ethylene glycol) were also found to play the role of a phase-transfer agent. However, the yield of **2e** are much lower (ca. 30–60%) (Table 4).

The yield of the cyclic carbonate **2** depends also on the CO_2 pressure in the reaction system. The yield is near to the theoretical at an initial pressure of 40 bar. However, when a comparatively low but constant CO_2 pressure during the reaction (of ca. 6 bar in the case of **1e**) is maintained, the yield of **2** is relatively high (Table 5).

Discussion

As appears from the results presented, the catalytic activity of alkali metal salts in the reaction expressed by Eq. (1) increases with an increase in the anion nucleophilicity and cation diameter. Complexation of the cation by a crown ether, *DABCO, TMEDA* or another phase-transfer agent, such as *TEBA*, facilitates the nucleophilic attack of the anion on the oxirane ring. In this work no simple correlation was found between the reactivity of oxiranes in the reaction (1) and their tendency to form hydrogen bonds[10]. However, it seems that such an attack of the anion toward the oxirane ring could be facilitated due to donor—acceptor interactions between the oxirane ring oxygen atom and the cation. Due to a considerable excess of the oxirane with respect to the crown ether in the systems studied, an oxirane interaction with the cation is possible, despite the stronger bonding of the cation by the ether. Such an interaction causing a decrease in electron density in the oxirane ring is more probable, since the reactions are carried out without a solvent which could compete with oxirane in the cation solvation. The oxirane ring opening due to the attack of the X^- anion can take place by the cleavage of the CH_2—O or CH—O bonds, depending on the kind of substituent *R* at that ring[11]. After opening of the oxirane ring and formation of a new alcoholate anion, according to Eq. (2 a, b) the CO_2 addition to that anion with the formation of a carbonate anion according to Eq. (3 a, b) takes place. This is followed by subsequent dioxolone ring formation (Eq. 4 a, b). The above reactions reflecting the proposed mechanism of formation of cyclic carbonate **2** from CO_2 and oxirane **1** are illustrated in the following scheme:



K$^+$ = crown ether complex.

In the systems studied the intermediate product of reaction (2a, b) (alcoholate anion) does not undergo further reaction with the oxirane where poly(alkylene oxide) could be formed. This results from the greater stability of the alkyl carbonate anion formed in the reaction (3a, b) than that of the initial alcoholate anion; thus this latter anion reacts easier with CO_2 (3 a, b) than with the oxirane. However, the oxirane polymerization products are formed in systems not containing CO_2 and when alkali metal salts giving not very strong nucleophiles (such as potassium carbonate, potassium monoalkyl carbonate, potassium carboxylate) activated with a crown ether are used[12]. In the systems studied also no poly(alkylene carbonate) is formed from the intermediate alkyl carbonate anion obtained in the reaction (3 a, b). This probably results from the anchimeric assistance taking place, and also due to the greater thermodynamic stability of the five-membered dioxolone ring formed from the cyclization of that anion (Eq. 4 a, b) with respect to the linear polycarbonate. Poly(alkylene carbonate)s can be obtained in the alternating copolymerization of CO_2 with oxiranes in the presence of coordination catalysts, the mechanism of which has been described elsewhere[13].

Experimental Part

The epoxides **1 a**, **b**, **d–f**, **i–k** were of commercial grade, **1 c** was obtained from the reaction of cyclohexene bromohydrin with a water solution of sodium hydroxide, **1 g** from that of 1,3-dibromopropanol-2 with calcium hydroxide[14] and **1 h** from that of 3-chloropropandiol-1,2 with phenylglycidyl ether in the presence of *TEBA*[15]. The epoxides **1** were dried prior to use by known methods. The alkali metal halides and carbonates were used after powdering and drying at 120 °C *in vacuo*. Potassium phenolates and carboxylates were obtained in known reactions with potassium hydroxide, applying azeotropic distillation to remove water from the reaction medium, and then dried at 130 °C *in vacuo*. Crown ethers: 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) were obtained as described in the literature[16]. Polyglymes were obtained from the reaction of the sodium salt of the respective poly(ethylene glycol) (commercial grade) with ethyl bromide. *TEBA*, commercial grade, *DABCO* and *TMEDA*, Fluka AG, were used without further purification.

General Procedure

To a 60 ml stainless steel pressure cylinder **1** and a respective amount of the catalyst were introduced, and then CO_2 from a gas cylinder was added at a ca. 1.5-fold greater amount by mole than **1**. The pressure cylinder was then closed and placed in a thermostated oil bath. In some cases CO_2 was introduced to the reactor under constant pressure during the reaction from a 40 l cylinder of a given CO_2 pressure. After completion of the reaction the pressure cylinder was cooled to room pressure, the excess of CO_2 was liberated and the product formed was washed to remove the catalyst with 10 ml of water (with the exception of **2 a**) and then distilled under reduced pressure. The yield of **2** was determined gravimetrically. The cyclic carbonates **2** obtained were characterized by means of elemental analysis (Perkin-Elmer model 240 microanalyser), ^{1}H-NMR spectroscopy (JEOL-C 100 H spectrometer, *TMS* being used as internal standard) and IR spectroscopy (film, Specord 71 IR-GDR). Boling or melting points (uncorrected), density and refractive index were also determined for those carbonates **2** (Table 6).

Table 6. *Data for cyclic carbonates* **2** *obtained in the reaction of* CO_2 *with epoxides* **1**

2	Formula	Mol. mass[a]	b.p.[b] °C/mm Hg	n^{25}	d g/cm³	^{1}H-NMR ($CDCl_3$) δ
a	$OC(O)OCH_2CH_2$	88.07	80–82/0.8[c]			4.46 (s) 4 H
b	$OC(O)OCH_2CHCH_3$	102.10	242–243		1.204^{20}	4.67 (m) 1 H; 4.09 (m) 2 H; 1.44 (d) 3 H
c	$OC(O)OCHCHCH_2CH_2CH_2CH_2$	142.17	116–118/0.4			4.67 (m) 2 H; 1.79 (m) 4 H; 1.46 (m) 4 H
d	$OC(O)OCH_2CHC_6H_5$	164.17	134–135/0.4	1.5312		7.29 (s) 5 H; 5.55 (m) 1 H; 4.44 (m) 2 H
e	$OC(O)OCH_2CHCH_2Cl$	136.44	108–109/0.4	1.4648	1.444^{18}	4.96 (m) 1 H; 4.40 (m) 2 H; 3.75 (m) 2 H
f	$OC(O)OCH_2C(CH_3)CH_2Cl$	150.47	124–126/1			4.26 (dd) 2 H; 3.65 (dd) 2 H; 1.62 (s) 3 H
g	$OC(O)OCH_2CHCH_2Br$	180.99	122–123/0.4	1.4968	1.828^{25}	4.94 (m) 1 H; 4.40 (m) 2 H; 3.59 (m) 2 H
h	$OC(O)OCH_2CHCH_2OH$	118.10	158–160/0.8			
i	$OC(O)OCH_2CHCH_2OC_4H_9$	174.22	124–125/0.5	1.4351		4.75 (m) 1 H; 4.37 (m) 2 H; 3.52 (m) 2 H; 3.39 (m) 2 H; 1.40 (m) 4 H; 0.82 (t) 3 H
j	$OC(O)OCH_2CHCH_2OCH_2CH{=}CH_2$	158.17	100–102/0.4	1.4519	1.173^{25}	
k	$OC(O)OCH_2CHCH_2OC_6H_5$	194.20	180–181/0.8[d]			7.01 (m) 5 H; 4.90 (m) 1 H; 4.41 (m) 2 H; 4.06 (m) 2 H

[a] All compounds gave satisfactory elemental analyses (C, H, Cl, Br); [b] b.p. uncorrected; [c] m.p. 35–36 °C; [d] m.p. 90–92 °C.

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