

Calcium chloride as co-catalyst of onium halides in the cycloaddition of carbon dioxide to oxiranes

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Abstract

The synthesis of 4-substituted 1,3-dioxolan-2-ones from the interaction between carbon dioxide and oxiranes in the presence of a catalytic system composed of tetraalkylammonium or phosphonium halide and calcium chloride has been investigated. It has been established that calcium chloride enhances the catalytic activity of the onium halides used. A mechanism describing the interaction between carbon dioxide and oxiranes has been suggested on the basis of the obtained experimental results. According to the assumed likely mechanism the catalytic system activates the oxirane and the opening of the oxirane ring is the rate-determining stage.

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Keywords: Cyclic carbonate; Carbon dioxide; Catalytic system onium halide–calcium chloride; Oxirane ring-opening

1. Introduction

Cyclic alkylene carbonates, derivatives of 1,3-dioxolane-2-one, are widely used as synthetic intermediates [1–3], in the polyurethane production [4,5] thus limiting the use of the toxic isocyanates. The synthesis of monomers bearing 1,3-dioxolan-2-one moieties and their polymerisation to polycyclic carbonates [6,7] have been investigated in respect to their potential applications as carriers of enzymes and cells [8,9] or reactive polymers [10], and as “host for dyes” in non-linear optics [11].

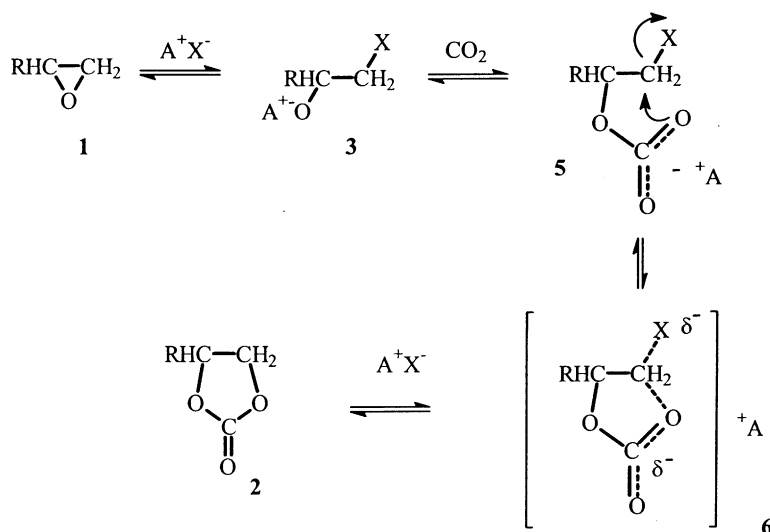
The preparation of cyclic carbonates by the addition reaction of carbon dioxide to oxiranes is a synthetic route involving safe and cheap starting materials

(carbon dioxide instead of toxic phosgene) [12]. Moreover, that is a convenient method for the preparation of alkylene carbonates, especially for industrial purposes [13]. The reaction does not proceed without a catalyst [14]. The alkaline and onium halides are the most often used catalysts promoting the reaction of carbon dioxide with oxiranes [15–17]. Generally, the reaction is performed at elevated CO₂ pressure (>40 atm) and high temperatures (between 120 and 200 °C, even higher, depending on the type of oxirane or catalyst). When other metal salts such as acetates, carbonates or bicarbonates were used, lower yields were obtained [17]. Kihara et al. [18] reported that only halides showed catalytic activity under atmospheric pressure and alkali metal halides were most effective in concentrations ≥ 5 mol% when the reaction was carried out in an aprotic dipolar solvent. With the purpose of increasing the yield of cyclic carbonate some reagents forming complexes with alkaline metal ions (crown

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ethers [19], polyethylene glycols [20]) were used as co-catalysts of the alkaline halides. Another catalytic system consisting of Mg-Al mixed oxides was also examined [21]. An electrochemical method based on the use of Ni(II) catalyst has been recently reported for the electrocarboxylation of epoxides [22].

Although good synthetic results have been achieved by the reaction of carbon dioxide with oxiranes in the presence of metal or onium halides, new, more effective and selective catalytic systems are still being examined. A possible route is the use of substances exhibiting co-catalytic activity and reacting reversibly with the reagents, for example the reaction between acids and bases. The starting oxiranes and the obtained carbonates are Lewis bases.

The generally accepted reaction mechanism (Scheme 1) involves several steps [17,23].

At first, an alcoholate anion is formed as a result of the opening of the oxirane cycle due to the catalyst attack on it. The obtained anion combines with a carbon dioxide molecule to form an alkylcarbonate anion. Then the attack of the carbonate anion on the β -carbon atom results in the formation of the carbonate cycle and catalyst regeneration. Though many catalyst systems have been examined, the structure (composition)–activity relationship of the catalytic species is still under discussion.

The purpose of the present study is to demonstrate the influence of calcium chloride, a Lewis acid, as co-catalyst upon the synthesis of alkylene carbonates from carbon dioxide and oxiranes in the presence of an onium halide as catalyst. Based on our findings we wish to postulate a reaction mechanism for the examined systems.

2. Experimental

2.1. Materials

1,2-Oxyranylethyl 2-propenoate, 1,2-oxyranylethyl 2-methyl-2-propenoate, 1,2-oxyranylethane, 1,2-oxyranylethane, 1-chloro-2,3-oxyranylethane—Fluka; tetrabutylammonium bromide (TBABr), triethylbenzylammonium chloride (TEBACl), tetraethylammonium iodide, trioctylmethylammonium chloride (Aliquot 336)—Merck were used without further purification.

2.2. Reaction procedure

The reactions were carried out in a 100 ml autoclave under 40 atm initial pressure of CO₂ which provided about or over 10% excess of CO₂ (depending

Table 1

Yields of 4-substituted 1,3-dioxolan-2-ones obtained by the reaction of the corresponding oxirane and carbon dioxide in the presence of TEBACl (1 mmol, procedure A) or TEBACl:CaCl₂ (2:1 mole ratio, procedure B) and 4 h reaction time

2	R	Procedure	Temperature (°C)	CO ₂ reacted (g)	Yield (g)	Yield (%)
a	CH ₃	A	170		3.90	8.9
		B	170		42.4	96.9
b	C ₂ H ₅	A	170		1.86	4.6
		B	170		36.4	90.75
c	ClCH ₂	A	100		6.70	12.8
		B	100		35.71	68.2
d	CH ₂ =CHC(O)OCH ₂	A	100	2.15	35.51 ^a	36.1 ^b , 36.2 ^c
		B	100	4.54	37.9 ^a	75.6 ^b , 76.4 ^c
e	CH ₂ =C(Me)C(O)OCH ₂	A	100	0.70	31.96 ^a	14.4 ^b , 14.4 ^c
		B	100	2.07	33.33 ^a	42.2 ^b , 42.3 ^c

^a The yield of the raw products **2d** and **2e** include the unreacted oxirane.

^b Determinate by HPLC.

^c Calculated on the basis of the quantity of CO₂ reacted.

on the molecular weight of the oxirane used). A 30 ml oxirane and the catalyst comprised of onium halide or onium halide–CaCl₂ were added to the autoclave. Then the reactor was filled with CO₂ at room temperature till the gas pressure reached 40 atm. The reaction temperature was increased and varied in the interval from 100 to 180 °C according to the type of reagents and catalysts used. The reaction mixture was vigorously stirred for a period of 2–8 h. Then, it was

cooled to room temperature and the unreacted oxirane was separated under vacuum. The type and amount of the oxirane and catalyst, as well as the reaction conditions applied in the different runs are pointed out in Tables 1, 2 and 4.

IR (a Bruker Vector 22 spectrometer), ¹H and ¹³C NMR spectroscopy (a Bruker 250 MHz instrument) and HPLC (performed on a RP8 column and eluent H₂O:MeOH = 1:1 at a flow rate 1.6 ml min⁻¹)

Table 2

Dependence of the yield of 4-methyl-1,3-dioxolane-2-one (**2a**) on the type of the catalytic system

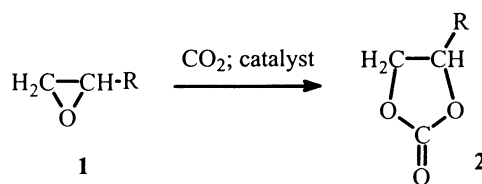
Catalytic system			Temperature (°C)	Time (h)	Yield of product	
Onium salt	CaCl ₂				g	%
Type	10 ⁻³ mol	10 ⁻³ mol				
		1.0	170	4	Trace	–
TEBACl	2.0	–	170	4	3.9	8.9
TEBACl	2.0	–	150	4	Trace	–
Aliquot	2.0	–	170	4	3.8	8.7
TBABr	0.5	–	150	4	11.02	25.18
TBABr	1.0	–	140	4	12.98	29.65
Ph ₃ PMeI	1.0	–	140	4	14.41	32.74
Et ₄ NI	1.0	–	140	4	11.72	26.62
TEBACl	2.0	1.0	170	4	42.4	96.9
Aliquot	1.0	1.0	170	8	42.87	97.4
TBABr	0.5	0.25	150	4	25.50	58.55
Ph ₃ PMeI	1.0	1.0	140	4	38.3	87.52
Et ₄ NI	1.0	0.5	140	4	34.4	78.6

were used to characterize the obtained 4-substituted 1,3-dioxolan-2-ones.¹

3. Results and discussion

The reaction between carbon dioxide and oxiranes yielding 1,3-dioxolan-2-ones (Scheme 2) has been investigated. The reaction was carried out in the presence of a catalytic system consisting of tetraalkylammonium or phosphonium halide and CaCl₂. Parallel to that, the interaction has been examined in the absence of CaCl₂. The starting set of reactions was performed with different oxiranes and triethylbenzylammonium chloride (TEBACl) as catalyst (Table 1, procedure A), while in the second one, a catalytic system comprised of TEBACl and CaCl₂ with a mole ratio 2:1, respectively, was used (Table 1, procedure B). The experimental results obtained are also listed in Table 1.

The unreacted oxiranes **1d** and **1e** cannot be easily separated from the reaction products due to their low volatility. Thus, for these trials the yields (in grams)



1, 2	R
a	CH ₃
b	C ₂ H ₅
c	ClCH ₂
d	CH ₂ =CHC(O)OCH ₂
e	CH ₂ =C(CH ₃)C(O)OCH ₂

Scheme 2.

of the raw products include the carbonate and the unconverted oxirane. The conversions (in percentage) of **2d** and **2e** have been calculated on the basis of the quantity of carbon dioxide reacted, as difference between the masses of the raw product and the starting oxirane. The data obtained from the ¹H NMR spectra of the crude products and the HPLC analysis are in good agreement (Table 1).

In all cases, CaCl₂ showed a pronounced co-catalytic activity. When oxiranes with a lower reactivity were used, this effect proved to be more pronounced. If the reaction temperature was lower than 130 °C then only trace quantities of carbonates **2a** and **2b** were obtained following both procedures A and B. This fact allows an assumption to be made that the addition of CaCl₂ does not cause a change in the reaction mechanism.

In order to prove that CaCl₂ is active as co-catalyst with various onium halides in the preparation of cyclic carbonates from CO₂ and oxiranes, the dependence of the yield of **2a** on the type of onium halide used has been examined. The obtained results are presented in Table 2. The relative catalytic activity of the onium halides (without co-catalyst) increases in the order Cl ≪ Br ≅ I. Conversions were less than 10% in the presence of both ammonium chlorides used, TEBACl and Aliquot 336, at 170 °C within 4 h reaction time. The yields increased as the temperature was raised to about 200 °C and the reaction time also became prolonged. However, this approach is hardly thought to be reasonable due to the fact that the selectivity of the reaction decreases with the increase in temperature.

¹ Spectral data for the products: 4-methyl-1,3-dioxolan-2-one (**2a**). ¹H NMR (CDCl₃): δ 4.91 (m, 1H CH), 4.01 (2d, *J* = 7.27 Hz, *J* = 8.55 Hz, CH₂), 1.46 (d, *J* = 5.98 Hz, CH₃); ¹³C NMR (CDCl₃): δ 18.31 (CH₃), 70.12 (CH₂), 73.27 (CH), 154.66 (C=O); IR: 3000, 1800, 1485, 1395, 1355, 1180, 1120, 1050, 770 cm⁻¹; 4-ethyl-1,3-dioxolan-2-one (**2b**). ¹H NMR (CDCl₃): δ 4.64 (m, 1H, CH), 4.50 (t, 1H, *J* = 8.1 Hz, CH₂-ring), 4.05 (2d, 1H, *J* = 8.4 Hz, *J* = 6.9, CH₂-ring), 1.68–1.82 (m, 2H, CH₂), 0.99 (t, 3H, *J* = 7.45 Hz, CH₂); ¹³C NMR (CDCl₃): δ 8.33 (CH₃), 26.77 (CH₂), 68.93 (CH₂), 155.07 (C=O); IR: 2971, 2938, 2882, 1798, 1660, 1554, 1463, 1378, 1302, 1180, 1112, 1062, 986, 917, 859, 776 cm⁻¹; 4-chloromethyl-1,3-dioxolan-2-one (**2c**). ¹H NMR (CDCl₃): δ 5.02 (m, 1H, CH), 4.61 (t, 1H, *J* = 8.5 Hz, CH₂), 4.41 (2d, 1H, *J* = 8.8 Hz, *J* = 5.8, CH₂) 3.67–3.87 (m, 2H, CH₂Cl); IR 2980, 2920, 1800, 1475, 1425, 1395, 1350, 1325, 1160, 1100, 1070, 1040, 760, 710 cm⁻¹; 2-oxo-1,3-dioxolan-4-ylmethylacrylate (**2d**). ¹H NMR (CDCl₃): δ 6.46 (dd, *J* = 17.2 Hz, *J* = 1.3 Hz, 1H, CH₂=CH-), 6.16 (dd, *J* = 17.2 Hz, *J* = 10.3 Hz, 1H, CH₂=CH-), 5.95 (dd *J* = 10.5 Hz, *J* = 1.3 Hz, 1H, CH₂=CH-), 5.04 (m, 1H, CH), 4.31–4.67 (m, 4H, CH₂); ¹³C NMR (CDCl₃): δ 165.15 (–C(O)O–), 154.35 (–OC(O)O–), 132.03 (–H₂C=CH–), 127.08 (–H₂C=CH–), 73.89 (CH); 65.95 (CH₂), 63.00 (CH₂); IR 2990, 1820, 1740, 1640, 1420, 1280, 1178, 1055, 980, 810 cm⁻¹; 2-oxo-1,3-dioxolan-4-ylmethylmethacrylate (**2e**). ¹H NMR (CDCl₃): δ 6.0 (s, 1H, CH₂=CMe-), 5.5 (s, 1H, CH₂=CMe-), 4.8–5.25 (m, 1H, CH), 4.15–4.25 (m, 2H, CH₂), 3.4–3.7 (m, 2H, CH₂), 1.8 (s, 3H, CH₃); IR 2990, 2970, 2930, 1800, 1745, 1640, 1450, 1395, 1290, 1160, 1095, 1050, 950, 805, 760 cm⁻¹.

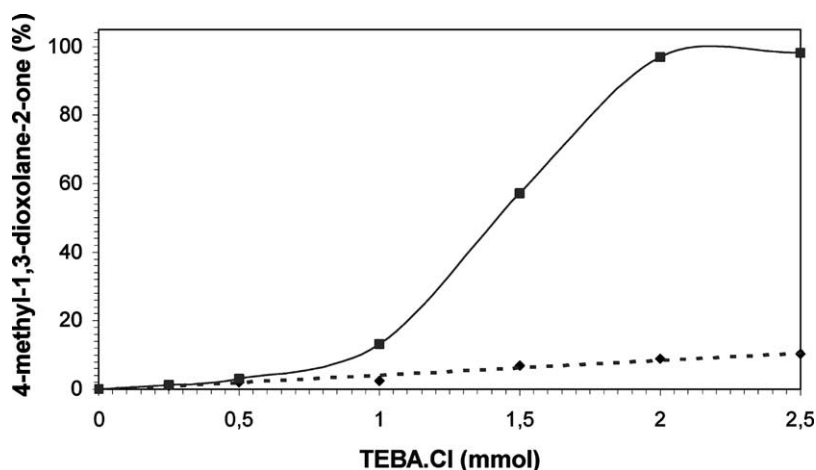


Fig. 1. Dependence of the yield of 4-methyl-1,3-dioxolane-2-one on the amount of triethylbenzylammonium chloride; reaction time 4 h, temperature 170 °C: (—) 1 mmol calcium chloride; (---) without calcium chloride.

The catalytic activities of the two iodides and the bromide studied are approximately the same and are considerably higher than that of the chlorides examined. The bromide, TBABr, used showed a catalytic activity between that of the two iodides. When ammonium iodide, Et₄N.I, was replaced by phosphonium iodide, Ph₃MePI, in the synthesis of **2a**, the yield of the product increased only by 6%.

In all cases, the application of the onium halide–CaCl₂ catalytic system led to a sharp increase of the reaction rate and the yield of carbonate in comparison with the halide used as sole catalyst. In the presence of tetraalkylammonium chloride–CaCl₂, the growth of the yield was about tenfold (Table 2). The quantity of **2a** doubled or trebled on addition of onium bromide–CaCl₂. Similar results were obtained with the mixture onium iodide–CaCl₂.

The influence of the composition of the catalytic system on the reaction course was demonstrated by the dependence of the yield of **2a** on the onium halide:CaCl₂ ratio.² The concentration of one of the

components of the catalytic system was kept constant while the quantity of the other one varied. In the absence of CaCl₂ (Fig. 1, dotted line), though a linear increase in the yield of **2a** with the TEBA.Cl concentration was observed, the yield did not exceed 10%. On addition of CaCl₂ (1 mmol, $3.33 \times 10^{-2} \text{ mol l}^{-1}$) to the reaction mixture, a dependence of another type was obtained (Fig. 1, solid line)—a small increase of the yield (although it was considerable in comparison with the yield obtained without CaCl₂) until an equimolar ratio of the two components was reached, followed by a sharp increase of the yield up to mole ratio TEBA.Cl:CaCl₂ = 2, and after that the yield decreased slightly despite of the further rise in the TEBA.Cl concentration.

The dependence of the yield of **2a** on varying the CaCl₂ amount (from 0 to 1 mmol, i.e. from 0 to $3.33 \times 10^{-2} \text{ mol l}^{-1}$, respectively) in the presence of TBABr (0.5 mmol, $1.67 \times 10^{-2} \text{ mol l}^{-1}$) is presented

² The correct discussion of the oxirane reactivity and the catalytic effect of the different systems used should be done on the basis of a comparison of the reaction rates or the rate constants measured in the presence of different catalysts. However, the kinetic measurements of such processes involve experimental and theoretical difficulties. In the first place, the experimental difficulties refer to the reaction conditions such as high pressure of CO₂, which in the beginning of the reaction was about 40 atm and grew

as the temperature increased. Under these reaction conditions, the removal of samples in the course of the process is difficult as well as the direct detection of properties related to kinetic parameters. Moreover, the reaction was performed without solvent and the polarity of the medium altered in the course of the process. Consequently, the kinetic parameters would depend on reaction time (conversion) and a relationship of the type $dC = Ak(t) dt$ should be employed in the kinetic model which additionally complicates the calculation and interpretation of the physical meaning of the obtained parameters.

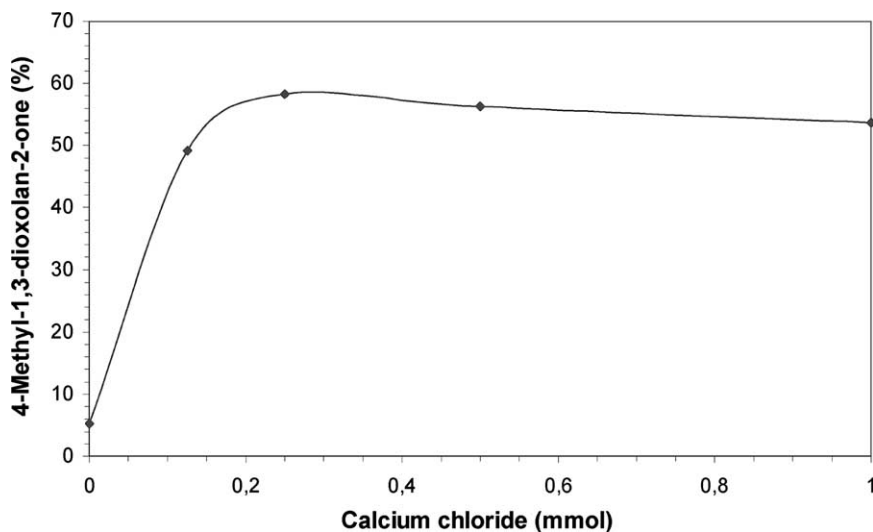


Fig. 2. Dependence of the yield of 4-methyl-1,3-dioxolane-2-one on the amount of calcium chloride; reaction time 4 h, temperature 170 °C; 0.5 mmol tetrabutylammonium bromide.

in Fig. 2. It confirms that the optimum proportions of the co-catalysts are at mole ratio onium halide:CaCl₂ = 2:1. This dependence was even better displayed when the TEBACl–CaCl₂ mixture was used (Fig. 3). CaCl₂ as co-catalyst enhanced the activity of onium

chloride to a greater extent than that of onium bromides or iodides. Moreover, the effect of the onium chloride–CaCl₂ pair cannot be explained by a simple addition of the catalytic effects of the components. Therefore, all results imply that under the reaction

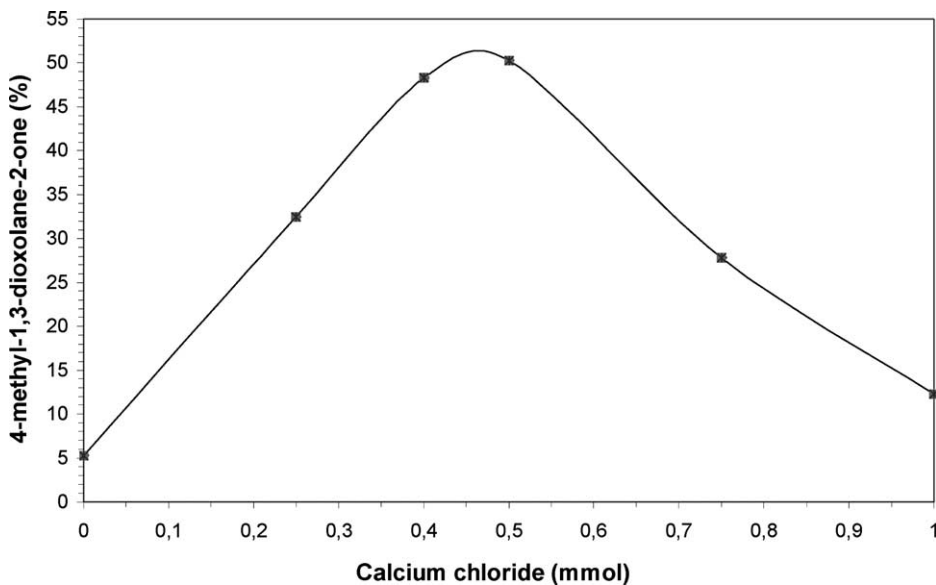


Fig. 3. Dependence of the yield of 4-methyl-1,3-dioxolane-2-one on the amount of calcium chloride; reaction time 4 h, temperature 140 °C; 1 mmol triethylbenzylammonium chloride.

conditions the components of the catalytic system interact yielding the active catalytic species.

Calcium chloride is a weak Lewis acid. It is also known that the coordination number of the calcium ion (i.e. the number of its nearest neighbors) is equal to or greater than six. On dissolving in an organic solvent, solvated molecules and ion-pairs as well as higher associates are formed. In the presence of onium halide, we assume, that the calcium ion or being more precise calcium chloride coordinates additional halogen ions and solvent molecules occupy the vacant sites. An experimental evidence for a strong interaction between calcium chloride and tetrabutyl ammonium chloride was found in the considerable frequency shift in the absorption maximum of $\nu(\text{Ca-Cl})$ observed on mixing the substances (Fig. 4). In the examined reaction system, the starting oxirane or the resulting carbonate act as solvents. The low volatility of propylene carbonate allowed infrared spectra of the mixtures to be performed easily in a thin layer. The calcium chloride spectrum was made in a KBr pallet due to its very low solubility in propylene carbonate.

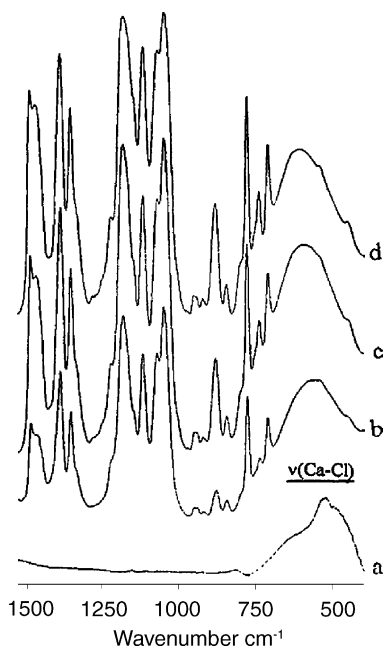


Fig. 4. Infrared spectra of calcium chloride (KBr pallet) and mixtures of calcium chloride and tetrabutylammonium chloride in 4-methyl-1,3-dioxolane-2-one (thin layer) in the region 1500–400 cm^{-1} : (a) CaCl_2 ; (b) $\text{TBACl}:\text{CaCl}_2 = 1:1$; (c) $\text{TBACl}:\text{CaCl}_2 = 2:1$; (d) $\text{TBACl}:\text{CaCl}_2 = 4:1$.

Table 3

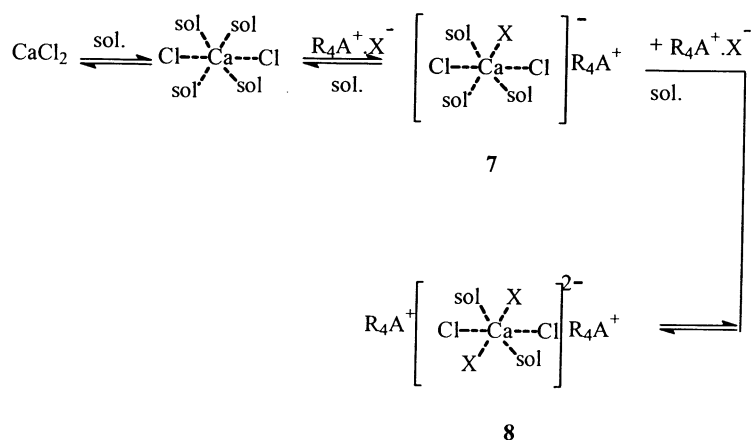
Shift in the absorption maximum of the Ca–Cl bond on mixing of calcium chloride and tetrabutylammonium chloride at different mole ratios in propylene carbonate at 22 °C

TBACl:CaCl ₂	$\nu(\text{Ca-Cl})$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
*	523	
1:1	580	57
2:1	606	83
4:1	617	94

It was observed, however, the calcium chloride solubility in propylene carbonate increased on addition of tetrabutyl ammonium chloride and a real solution was obtained at mole ratio $\text{TBACl}:\text{CaCl}_2 = 2$ and ambient temperature—another indirect proof that the components of the catalytic system interact and new soluble species are formed. The shift in the maximum for the Ca–Cl band increases with the increase of the onium salt excess and it is in direction towards higher wavenumbers (Table 3). This is an indication that the order of the bond enhances and stable species are formed. A simplified scheme (Scheme 3) of this interaction is suggested not accounting for the formation of higher molecular/ionic associates in the solution.

It has been assumed [17,23], that the attack of the alkylcarbonate anion on the β -carbon atom during the stage of the carbonate cycle formation is the rate-determining step of the interaction between CO_2 and oxiranes in the presence of alkaline or onium halides as catalysts (Scheme 1). The assumption is in accordance with the generally held view about the relative rate of the bimolecular nucleophilic substitution reactions. The low nucleophilicity of the carbonate anion and the high reactivity of the oxirane cycle towards nucleophiles are arguments for the above suggestion. A mechanism, also considering the alkylene carbonate ring formation to be the rate-determining stage, has been presumed for the same reaction promoted by ion-exchange resins containing quaternized ammonium or phosphonium groups [24].

In this study, we endorse the alternative view, i.e. the opening of the oxirane ring to be a rate-determining step. The presence of calcium ions in the system means that they would interact with the carbonate ions of **5** more strongly than with the halide ion eliminated during the cycle formation. Therefore, the nucleophilicity of the carbonate group in **5** would decrease due to its coordination with the calcium atoms, while the energy

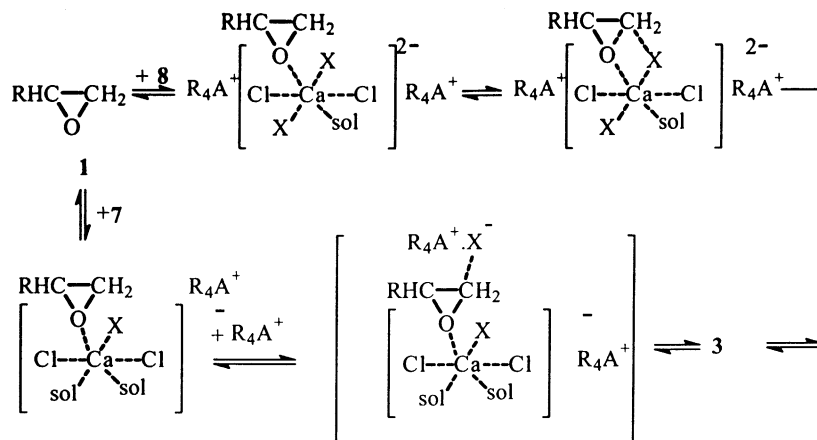


Scheme 3.

of the transition state **6** would increase compared to **5**. As a result, the reaction rate should be lower in the presence of CaCl_2 than it is without adding CaCl_2 . What is more, the reaction of alcohols with CO_2 is a fast process and under alkaline conditions it is an irreversible reaction [25]. Consequently, the equilibrium of the second stage is shifted towards the substituted carbonate **5** possessing a halogen in the β -position.

The experimental data obtained in this study can be explained assuming the rate-determining step to be the first one, namely the opening of the oxirane ring on catalyst attack. In that case (Scheme 4), the coordination of the calcium atom from the catalyst **7** or **8** with the oxygen atom of **1** through a donor-acceptor bond

results in the polarization of C–O bonds in **1**. A particular consideration deserves the fact that the maximum catalytic activity is observed in the presence of onium halide: CaCl_2 in mole ratio 2:1. Two hypotheses considering two limiting cases have been suggested to explain the observed relation: (i) the active species is a complex formed between CaCl_2 and two molecules onium halide **8**, and then the reaction is accomplished following path “a” and the ring-opening takes place in the calcium coordination sphere; (ii) the oxirane reacts with an equimolar complex **7**, and the ring-opening is realized upon the attack of a halogen ion from a second halide molecule (path “b”). The geometry of both possible transition states is given in Scheme 4.



Scheme 4.

Table 4

Yields of 4-substituted 1,3-dioxolan-2-ones obtained under optimized reaction conditions

2	R	Catalytic system			Temperature (°C)	Time (h)	Yield of product (%)
		Onium salt		CaCl ₂			
		Type	10 ⁻³ mol	10 ⁻³ mol			
a	CH ₃	TEBACl	2.5	1.0	170	4	>98
		Aliquot	1.0	1.0	170	8	97.4
		TBABr	1.0	–	170	4	97.4
		TBABr	1.0	0.5	150	8	>98
		Ph ₃ PmePI	2.0	1.0	140	6	>98
b	C ₂ H ₅	TEBACl	2.0	1.0	170	8	>98
		Aliquot	2.0	1.0	170	5	98.3
c	ClCH ₂	TEBACl	2.0	1.0	120	8	>98

Unfortunately, the experimental results do not allow one of the reaction paths to be preferred to the other.

Despite the differences in the catalytic activity of the systems examined in this study, experimental conditions can be found under which the corresponding carbonate **2** will be prepared in a sufficiently high yield. Table 4 includes data about some catalytic systems and the yields of 4-substituted 1,3-dioxolan-2-ones obtained under optimized reaction conditions (temperature, reaction time, and catalyst concentration). The presented results demonstrate that the interaction between the carbon dioxide and oxiranes under the examined conditions proceeds without side reactions.

4. Conclusions

It has been found that calcium chloride shows a pronounced co-catalytic effect in the synthesis of 4-substituted 1,3-dioxolan-2-ones from the reaction between carbon dioxide and oxiranes in the presence of tetraalkylammonium or phosphonium halides. The application of the catalytic system allows the interaction to be performed at lower temperatures. A mechanism of the reaction between carbon dioxide and oxiranes is suggested. It is assumed that the opening of the oxirane ring activated by the catalytic system is the rate-determining step.

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