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# SYNTHESIS OF CYCLIC ALKYLENE CARBONATES AT LOW TEMPERATURES AND PRESSURES

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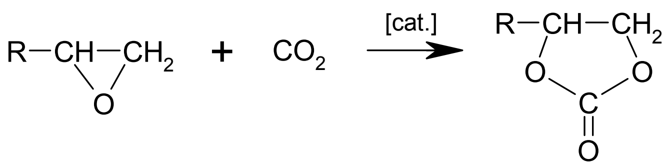
**Abstract**

The addition of $CO_2$ to propylene oxide (methyl oxirane) was used to examine the effect of catalytic systems formed from Lewis bases, mainly N,N-dimethylformamide (DMF) and tributylamine (TBA), and preferentially halides of transition metals of the iron triad ($CoCl_2$, $FeCl_3$ and $NiCl_2$) and some Group 2 metal halides ($CaCl_2$, $MgBr_2$, $ZnCl_2$, $CaI_2$, and $SnCl_2$) on the conversion of the addition and its selectivity to propylene carbonate formation (PC). The use of the hydrates of these halides and moisture in the reactants decrease PC selectivity. Almost quantitative conversion of propylene oxide can be achieved at a nearly optimum temperature of 120 $\pm$ 2 °C and a total pressure of 3-4 MPa. Selectivities to PC ranged from 82 to 94% were obtained with DMF-$CoCl_2$ >DMF-$NiCl_2$ > DMF-$CaI_2$ >DMF-$CaBr_2$, followed by DMF-$ZnCl_2$, DMF-$CaCl_2$, DMF-$FeCl_3$ and DMF-$SnCl_2$. NaCl, NaBr, and $CuCl_2$ were inactive, as well the low active and nonselective were Co, Ni, Fe and Ca carboxylates, nitrates and carbonates. The positive effect of $CO_2$ pressure in the range of 1-3 MPa on the selectivity of the addition to cyclic alkylene carbonates at 120 $\pm$ 2 °C was confirmed with 6 different epoxy compounds, as documented e.g. by the data obtained with DMF (68,4 mmol)-$CaCl_2$ (7.39 mmol) system: at 6-8 MPa and almost quantitative PO conversion, PC selectivity was 62% while at 2-3 MPa PC equaled to 92%. With butene oxide, the selectivity to butylene carbonate was 58%, at 7-9 MPa, while at 1-2 MPa PC amounted to 92%. A similar positive effect of lower pressure was confirmed also in the case of other epoxy compounds.

**Keywords:** *cyclic alkylene carbonates, alkene oxides, carbon dioxide, mild pressure, mild temperature.*

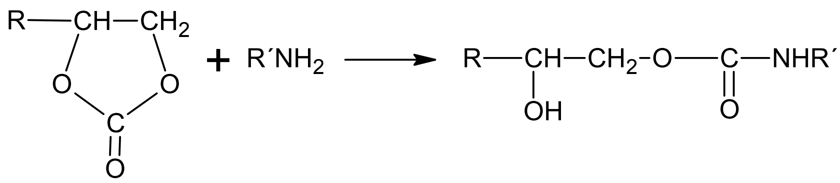
## 1. Introduction

Cyclic alkylene carbonates (1,3-dioxolane-2-one derivatives) produced by base-catalyzed insertion of carbon dioxide into alkylene oxides (oxirane and alkyl oxiranes)




$\Delta H$ = - 96,3kJ/mol (1)

(R= H, alkyl, alkenyl) are widely used as solvents and extractants, and particularly as reactive intermediates [1-18]. It is also known to use alkylene carbonates for isocyanate-free synthesis of urethanes [4,11-14].



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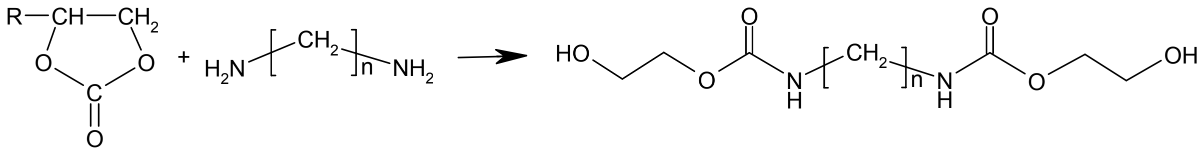
and reactions with diamines and diols to produce polyurethanes [13-17,26] has long been of special interest.



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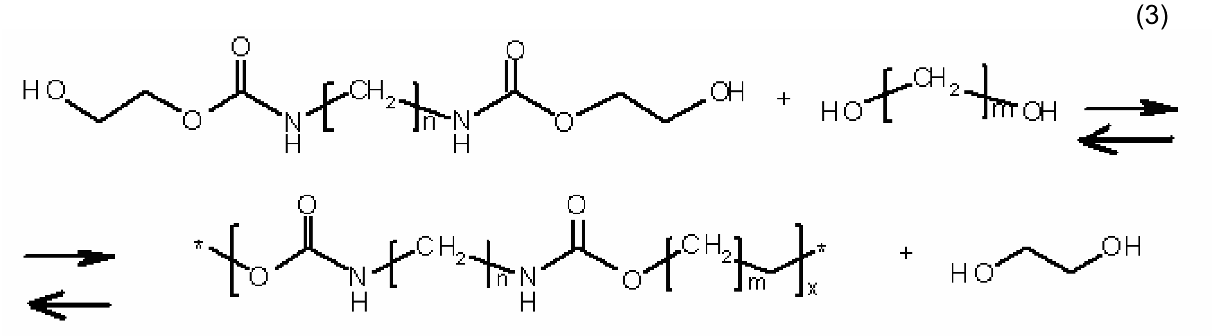

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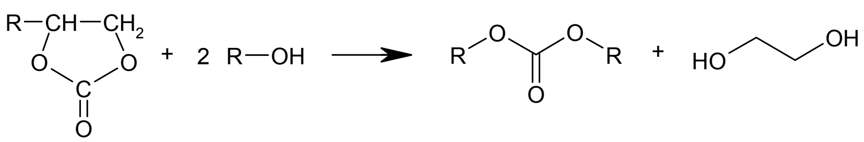
The synthetic utility of alkylene carbonates further extends by their potential application as intermediates for the production of polycarbonates and glycols + dialkylcarbonates [23-25]. Thus, the reaction of ethylene carbonate with methanol yields dimethyl carbonate and ethylene glycol



(5)

where R denotes methyl group, ethyl, or other alkyl group.

Similarly, its reaction with ethanol gives diethyl carbonate and ethylene glycol. Both carbonates may be used as high-octane components of gasoline. The producers of oxirane and alkyl oxiranes thus get the opportunity to further expand the utilization of environmentally problematic carbon dioxide.

Cyclic alkylene carbonates have been prepared by several procedures [4-7,11-20], but the insertion of carbon dioxide into alkene oxides is preferred, in spite of rather severe reaction conditions (120 - 200°C, or 165 - 245°C[18] and 4.3 to 15 MPa pressure). The first catalyst for the synthesis of propylene carbonate was sodium hydroxide deposited on activated carbon [3]. The yield of the carbonate was however low due to a rapid deactivation of the hydroxide by its conversion to sodium carbonate with carbon dioxide. The higher yields were obtained with alkali earth carbonates, bicarbonates and halides [18], and especially quarternary salts and tertiary amines as catalysts [18-21] at 100°C (or 140 – 200°C) and 4 - 20 MPa. To date, a number of other compounds have been found to be catalytically effective: quarternary ammonium salts [21], tetralkylammonium organotin halides [5,18-22], metal phthalocyanines with metals in both low and high oxidation states [18-22], alkali earth and transition metals (especially Co, Ca, Cr, Fe, Ni and V) as metal components, metalloporhyrines with amines [6,151819], complexes of 4b and 5b metals with Lewis acids[29], including trialkyl- and triarylphosphines [27-29], a two-component system containing N,N-dimethylformamide as Lewis base and metal halides as activators [29] or cocatalysts. Similar results as with propylene oxide were also obtained with other alkylene oxides [27,32].

The following procedures are also worth mentioning: the synthesis of alkylene carbonates from alkylene oxides and carbon dioxide at 140 - 200°C [29,31] catalyzed by phosphonium and some inorganic halides [34]. A recently patented process [35] describes the use of a heterogeneous polyacid [36]. Other catalysts are of the general formula $L_mMX_n$ where L is selected from the group of pyridines, M is metal atom, selected from Zn, Fe, Mn, Pb, and In; X is Cl, Br or I, m is 1 or 2 and n is 2 or 3. A similar catalytic system [36] containing a metal complex [$MX_m$] with coordinated pyridine or its derivative [Py], where M is metal (Zn, Fe, Mn, Pb, In] and X is Cl, Br , I, m is 2 or 3. These systems are based on the experience with the previous ones [39,40].

In connection with our previous results [32] and some important studies of other authors the aim of the present work has been to find efficient cocatalysts of the system containing N,N-dimethylformamide or tributylamine as Lewis bases, using mainly propylene oxide as a model alkylene oxide.

## 2. Experimental

### *2.1 Chemicals*

Methyl oxirane (Propylene oxide, PO), produced by Novacke chemicke zavody, a. s., Novaky, SR and containing 0.013 mass % water (determined by the Fischer method) was redistilled and dried over zeolites to the final purity of 99.99 wt. %. Ethylene oxide (oxirane), chemical grade, was redistilled and contained 0.015 wt. % water. N.N-Dimethylformamide (DMF) ,chemical grade, was distilled and contained 0.28 wt. % water. Tributylamine (TBA) , 99.5% purity was distilled before use.

Other alkylene oxides and their derivatives (butylene oxide, cyclohexane oxide, 1,2-epoxyoctadecane, 3,4-epoxy-but-1-ene, epichlorhydrin), chemical grade, were dried before use over zeolites and then distilled to > 99.2 wt. % products.

Metal halides, sulfates and acetates, used as catalysts or co-catalysts of the system containing N,N-dimethylformamide were of analytical grade. Carbon dioxide (food grade), purity 99.8 wt. % .

### *2.1 Procedure*

A stainless steel autoclave (volume 125 $cm^3$) equipped with a temperature control and a propeller stirrer was charged with 5.0 g of N,N-dimethylformamide, or tributylamine, 15 g of propylene oxide (or other alkylene oxides tested) and different types of cobaltous, ferrous and other metal salts were added in the amounts which did not exceed their solubility in the reaction system. Then, the autoclave was closed, cooled to temperature close $0^oC$, flashed thre times with nitrogen and then pressurized with carbon dioxide to 2-2.5 MPa. The stirred reaction mixture was then warmed up to the required reaction temperature that was maintained with the accuracy of $\pm 2^oC$. The experiment lasted usually 3 h. The temperature and pressure were recorded in 5 min. intervals. When the pressure decreased below 1-2 MPa, the autoclave was re-pressurized with carbon dioxide to the upper working pressure. After completion of the reaction, the content of the autoclave was rapidly cooled to room temperature and the product withdrawn, weighed and analyzed by GC. The alterations to the just described procedure are mentioned in the appropriate place in the Results and discussion.

GC analyses were carried out on a Chrom 5 gas chromatograph (Laboratorni pristroje, Prague) using a 2.5 m - column (3 mm i.d.) packed with 5 % Carbowax 20 M on Chromaton G-A-W-DMSC. Column temperature = $150^oC$, the temperature of flame ionization detector and inlet port = 250 $^oC$, the flow rates of hydrogen, air and nitrogen were 40 $cm^3$/min, 30 $cm^3$/min and 25 $cm^3$/min , resp. The analyses of the reaction mixtures were made by the method of internal standard, using butanol in the most cases. Under the above described conditions the retention times (in min) of individual components were as follows: propylene oxide – 1.4, butanol- 2.4, N,N-dimethylformamide- 5.6, propylene glycol- 16.5, propylene carbonate- 27.3, and dipropylene glycol- 39.2.

The higher alkylene carbonates and propylene glycol oligomers were analyzed by HPLC (Schimadzu LC 20 instrument, a 30 cm –column (7.8 mm i.d. ) packed with TSK-GEL, G-OLIGO-PV, using distilled water- acetonitrile or methanol as mobile phase ($40^oC$, refractometric detector (RID)).

## 3. Results and discussion

We first examined the effect of selected metals as cocatalysts on the course of the model reaction of propylene oxide with carbon dioxide. The reaction was carried out at the temperature of $120 \pm 2^oC$, which is supposed to be optimal [32]. Initial carbon dioxide pressure was of 2.5 MPa and reaction time of 3 h. The conversions of PO and selectivities to propylene carbonate (4-methyl-1,3-dioxolan-2-one) formation (PC) and propylene glycol (PG) in dependence on $CoCl_2.6H_2O$ mol. ratio are shown in Figure 1. The results show that already at a ratio 4.9 mmol $CoCl_2.6\ H_2O$ to 1 mol of PO, the PO conversion was virtually quantitative and PC selectivity ($S_{PC}$) exceeded 60 %. Then, $S_{PC}$ increases up to 93 % at the 0.0195 molar ratio of the cobalt salt to PO and then steeply decreases, as shown in Fig. 1.

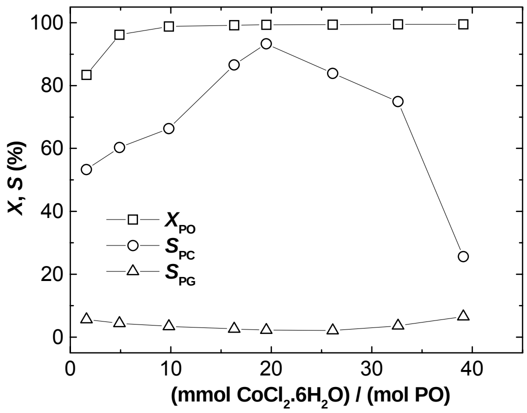



Fig. 1 Dependence of PO conversion (X) and selectivity (S) of the reaction to propylene carbonate ($S_{PC}$) and to propylene glycol moieties ($S_{PG}$) on the amount of the cocatalyst in the system DMF-$CoCl_2$.6 $H_2O$ at 120 ± 2°C and reaction time 3h

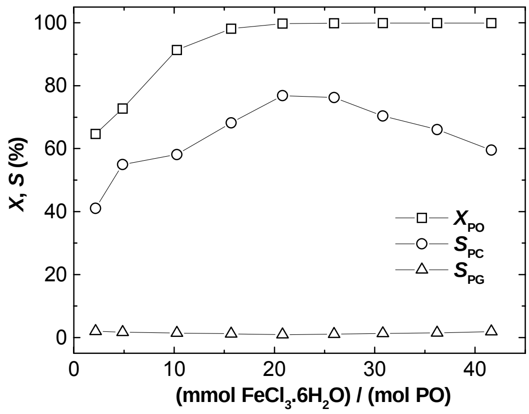



Fig. 2 Dependence of PO conversion (X) and selectivity (S) of the reaction to propylene carbonate ($S_{PC}$) and to propylene glycol moieties ($S_{PG}$) on the amount of $FeCl_3$.6 $H_2O$ in the catalytic system with DMF (120 ± 2°C , 2.5 MPa $CO_2$ pressure and reaction time 3 h)

This decrease can be attributed mainly to side reactions, especially that of PO with water to PG which in turn reacts with PO to give dipropylene glycol and propylene glycol oligomers. This conclusion is supported by the fact that the consumption of carbon dioxide decreases with increasing amount of $CoCl_2$.6 $H_2O$, which indicates that carbon dioxide does not participate in the decrease in PC selectivity for which the already mentioned reaction of PO with water to PG and its subsequent propoxylation are responsible. Under similar reaction conditions, the use of $FeCl_3$.6 $H_2O$ as co-catalyst led to very similar results, as reported in Fig. 2.

The PO conversion and PC selectivity increase with increasing amount of the ferric salt up to 0.02606 molar ratio $FeCl_3$.6 $H_2O$ to PO at which $S_{PC}$ attains 77.1 % and then distinctly decreases. Similarly, to the cobalt catalysis, also here this selectivity decrease is accompanied by the increased formation of PG and its oligomers.

Under similar reaction conditions, the use of anhydrous $CaCl_2$ as catalyst led to the results analogous to those found by us earlier with $CoCl_2$ [32]. Fig. 3 shows that PO conversion increases with increasing amount of $CaCl_2$, but even at 23 % PO conversion the PC selectivity is only 3%. At practically quantitative PO conversion, PC selectivity attains 64 % at 0.021 molar ratio $CaCl_2$ to PO, then increases up to 83.5 % attained at 0.029 molar ratio $CaCl_2$ to PO, remaining practically unaffected by further increase of $CaCl_2$ to PO molar ratio (Fig. 3).

While at 53.4% PO conversion PC selectivity was 3.1% and PG 1.6 %, the rest of PO reacted to mainly dipropylene glycol (DPG), PO oligomers and other side products. Dihydroxypropyl carbonates, terpolymers or copolymers of $CO_2$ with propylene oxide[41] are the most probale representatives of these side products. At 21 mmol $CaCl_2$ (99.2 % PO conversion) the PC selectivity was 83.5 % but the PG selectivity only 0.01 %. PG was not detected among reaction products at the greater $CaCl_2$ amounts. In addition to PO, DPG and PG oligomers, also water present in the reactants is responsible for formation of PG, DPG , propylene glycol oligomers, and other side products.

The results also show that under given experimental conditions the hydration of PO to PG and DPG and the above mentioned reaction of PC with PG to dihydroxypropyl carbonate prevail over the addition of carbon dioxide to PO. But, as soon as the water is consumed, essentially the only processes, which can take place are the insertion of $CO_2$ into PO and the reaction of PO to PG, dimers and oligomers. Comparison of the efficiency of some metal cations as components of the catalytic system is shown in Table 1.

The results show that the high catalytic activity for the insertion of carbon dioxide into PO is displayed not only by transition metal halides, but also by some Group 2 elements. The low activity of CuCl2 is most likely due to its sparse solubility in the reaction mixture. DMF-NaCl did not catalyze this reaction.

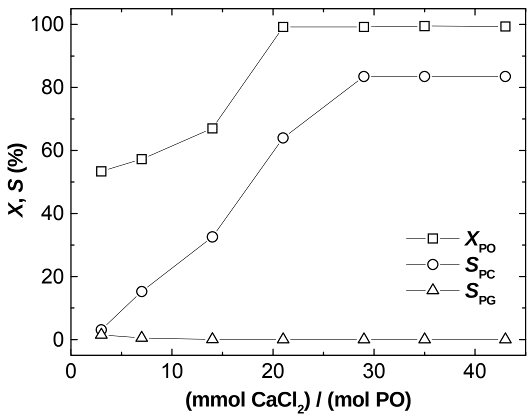



Fig. 3 Dependence of PO conversion (X) and selectivity (S) of the reaction to propylene carbonate ($S_{PC}$) and to propylene glycol moieties ($S_{PG}$) on the amount of $CaCl_2$ in catalytic DMF-$CaCl_2$ system(120 ± 2°C , 2.5 MPa $CO_2$ pressure and reaction time 3 h).

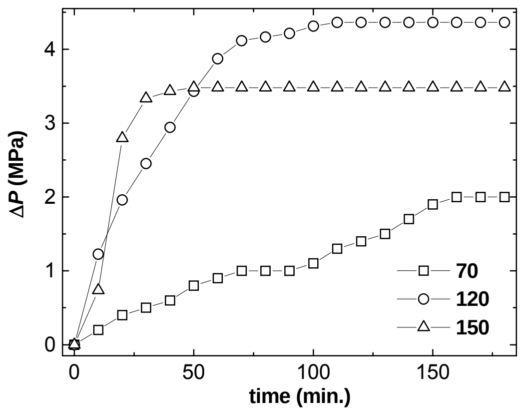



Fig. 4 Time dependence of pressure decrease (□P) in the synthesis of PC (for reaction conditions see Table 3)

Table 1 Efficiency of some metal cations in metal halides as components of the catalytic system with DMFA on PO conversion ($X_{PO}$) and selectivity to PC ($S_{PC}$) and PG ($S_{PG}$) in experiments carried out at 120 ± 2°C and initial carbon dioxide pressure of 2.5 MPa for 3 h ( 4.86 x $10^{-3}$ mmol metal)

| Metal halide | $X_{PO}$ [%] | $S_{PC}$ [%] | $S_{PG}$ [%] |
|---|---|---|---|
| $CoCl_2.6\ H_2O$ | 99,8 | 93,3 | 2,2 |
| $CoCl_2$ | 99,9 | 94,3 | 0,5 |
| $NiCl_2.6\ H_2O$ | 99,5 | 87,6 | 1,5 |
| $NiCl_2$ | 99,8 | 90,5 | 0,7 |
| $FeCl_3.6\ H_2O$ | 99,5 | 70,8 | 0,9 |
| $FeCl_3$ | 99,6 | 71,3 | 0,05 |
| $SnCl_2.2\ H_2O$ | 94,9 | 71,2 | 3,5 |
| $SnCl_2$ | 96,6 | 71,4 | 0,7 |
| $ZnCl_2$ | 99,97 | 90,6 | 0,05 |
| $CuCl_2.2\ H_2O$ | 38,9 | 20,3 | 8,2 |
| $CuCl_2$ | 41,9 | 23,3 | 0,6 |
| NaCl | 44,2 | 0,0007 | 0,01 |
| NaBr | 48,3 | 0,0 | 1,4 |
| $MgCl_2.6\ H_2O$ | 61,4 | 55,6 | 1,4 |
| $CaCl_2.2\ H_2O$ | 97,4 | 74,8 | 0,3 |
| $CaCl_2$ | 99,7 | 82,5 | 0,4 |
| $CaBr_2$ | 99,9 | 89,5 | 0,1 |
| $CaI_2$ | 99,9 | 90,0 | 0,1 |
| $CaCl_2$[a] | 99,6 | 89,6 | 3,6 |
| $CaCl_2$[b] | 92,1 | 93,5 | 3,5 |

*Reaction times were [a] 2.25 h and [b] 2.0 h.*

The fact that halides of some transition and Group 2 metals form efficient catalytic systems with DMF for the addition of $CO_2$ to akylene oxides has inspired us to evaluate also the effect of these metal salts anions. The exploratory experiments were carried out under the conditions identical to those described in Table 2 (the same metal amounts, 120 ± 2°C , inititial $CO_2$ pressure = 2.5 MPa, reaction time = 3 h) . The results are given in Table 2.

It becomes evident that contrary to Co, Ni, Ca, Mg and Mn halides, the carboxylates, nitrates, carbonates and sulfates are essentially inactive as the catalysts of the DMF-metal salt system for the addition of $CO_2$ to PO and likely also to other alkene oxides. This conclusion was inferred from the fact that the $CO_2$ pressure remained constant during these experiments and the only reactions taking place were the side reactions of PO.

Table 2 Effect of metal salt anions in the catalytic system with DMF on PO conversion and PC selectivity

| Potential catalyst | $X_{PO}$ [%] | $S_{PC}$ [%] | $S_{PG}$ [%] |
|---|---|---|---|
| $(CH_3COO)_2Ca$ | 31,7 | 0,003 | –- |
| $(HCOO)_2Ca$ | 50,1 | 0,055 | 2,05 |
| $(CH_3COO)_2Co$ | 48,6 | 0,201 | –- |
| $CoCO_3$ | 30,9 | 0,003 | 10,68 |
| $Co(NO_3)_2.6\ H_2O$ | 49,0 | 0,202 | –- |
| $MgSO_4.7\ H_2O$ | 43,6 | 0,029 | 6,08 |
| $(CH_3COO)_2Mn$ | 37,3 | 0,215 | 10,28 |
| $(CH_3COO)_2Zn.2\ H_2O$ | 46,6 | 0,027 | 2,24 |

The reaction temperature around 120°C was found most suitable for the addition of $CO_2$ to epoxy compounds, which is in accordance with our previous experiments [32]. In order to verify this finding again, we examined temperature effect with the MDF-$CaCl_2$ system. Temperature dependence of PO conversions and PC selectivities are presented in Table 3 and the pressure changes in dependence on reaction time and temperature are represented graphically in Fig. 4.

Table 3 Effect of temperature on the synthesis of PC by the addition of $CO_2$ to PO catalyzed by DMF-$CaCl_2$ system[a]

| Temperature [°C] | $X_{PO}$ [%] | $S_{PC}$ [%] | $S_{PG}$ [%] |
|---|---|---|---|
| 70 ± 1 | 41,5 | 0,2 | 7,3 |
| 120 ± 1 | 99,2 | 83,5 | 0,6 |
| 150 ± 1 | 93,6 | 81,0 | 2,4 |

*[a]125 $cm^3$ autoclave was charged with 15 g PO, 5 g DMF and 0.82 g $CaCl_2$; $CO_2$ pressure= 2.5 MPa, reaction temp. = 120 ± 2°C, 3 h*

We have thus proved that for the addition of $CO_2$ to PO catalyzed by DMF-$CaCl_2$ the reaction temperature around 120°C is suitable with respect to both the selectivity of the reaction to PC and the reaction rate. At 70° C the rate of the addition is slow and the hydration of PO and the propoxylation of PG become dominant processes. Results obtained at 150°C show that not only the selectivity to PC but also the rate of the addition decreases.

We have also determined the suitable amount of DMF as Lewis base in the system with $CaCl_2$ by changing the amount of DMF at a constant amount of $CaCl_2$ (7.39 mmol $CaCl_2$, i.e. 5.47 wt. % / PO) . The results are summarized in Table 4 and show that not only PC selectivity, but also the yield of PC are highest at the amounts of DMF and $CaCl_2$ of 20.5 mmol and 7.39 mmol to 1 mol of PO, resp. Moreover, the reaction rate was even higher than that achieved with the use of the twofold amount of DMF. A similar dependence was also found with $FeCl_3.6\ H_2O$ + DMFA system.

Table 4 Effect of the amount of DMF as component of the catalytic system containing a constant amount of $CaCl_2$ (7.39 mmol) in the addition of $CO_2$ to PO at 120 ± 2°C, $CO_2$ pressure 2MPa and reaction time 3h

| DMF | | $X_{PO}$ [%] | Selectivity | |
|---|---|---|---|---|
| [mmol] | [wt. % per PO] | | $S_{PC}$ | $S_{PG}$ |
| 20,5 | 10,0 | 84,3 | 64,3 | 0,3 |
| 68,4 | 33,3 | 99,2 | 83,5 | 0,8 |
| 205,2 | 100 | 98,9 | 62,0 | 5,0 |

This indicates that the optimum amount will be higher than 20,5 mmol (10 wt. % /PO) but lower than that the most frequently used by us (68,4 mmol, DMF/PO mol. ratio = 0.8, i.e. 100 wt.%/PO).

With regard to the need of supercritical $CO_2$ temperature for its selective addition to alkene oxides, we have tested the effect of total $CO_2$ pressure on the addition to PO catalyzed by DMF-$CaCl_2$ and DMF-$FeCl_3$ , using the same molar amounts at 120 ± 2°C and reaction time 3 h. The data listed in Table 5 show that in the presence of both catalytic systems the reaction rates do not practically depend on the initial $CO_2$ pressure (1 to 5 MPa) while, on the other hand, the selectivity to PC formation is pressure-dependent.

**Table 5** *Effect of initial $CO_2$ pressure (at 25°C) on the rate of PO addition, PO conversion and PC selectivity at 120 ± 2°C and reaction time 3 h with DMF-$FeCl_3$, DMF-$CaCl_2$, and DMF-$MgBr_2$*

| Initial $CO_2$ pressure [MPa] | Catalytic system | $X_{PO}$ [%] | $S_{PC}$ [%] | $S_{PG}$ [%] |
|---|---|---|---|---|
| 1 | DMF-$CaCl_2$ | 99,7 | 94,5 | 0,3 |
| 2 | DMF-$CaCl_2$ | 99,6 | 83,5 | 0,3 |
| 3 | DMF-$CaCl_2$ | 99,7 | 74,8 | 0,3 |
| 4 | DMF-$CaCl_2$ | 99,6 | 73,3 | 0,3 |
| 5 | DMF-$CaBr_2$ | 99,9 | 79,8 | 0,2 |
| 1 | DMF-$FeCl_3$ | 100 | 81,1 | –- |
| 2 | DMF-$FeCl_3$ | 100 | 77,7 | –- |
| 3 | DMF-$FeCl_3$ | 99,6 | 71,3 | 0,04 |
| 4 | DMF-$FeCl_3$ | 99,3 | 70,8 | 0,07 |
| 5 | DMF-$FeCl_3$ | 99,2 | 70,2 | 0,08 |
| 6 | DMF-$FeCl_3$ | 99,4 | 76,6 | 0,23 |
| 1 | DMF-$MgBr_2$ | 99,8 | 92,3 | 0,1 |
| 2 | DMF-$MgBr_2$ | 99,7 | 86,3 | 0,3 |
| 3 | DMF-$MgBr_2$ | 100 | 84,8 | 0,4 |
| 4 | DMF-$MgBr_2$ | 100 | 83,1 | 0,8 |
| 5 | DMF-$MgBr_2$ | 100 | 82 | 1,3 |

The effect of initial $CO_2$ pressure (at room temperature) on PC selectivity for the various catalytic systems is shown in Fig. 5

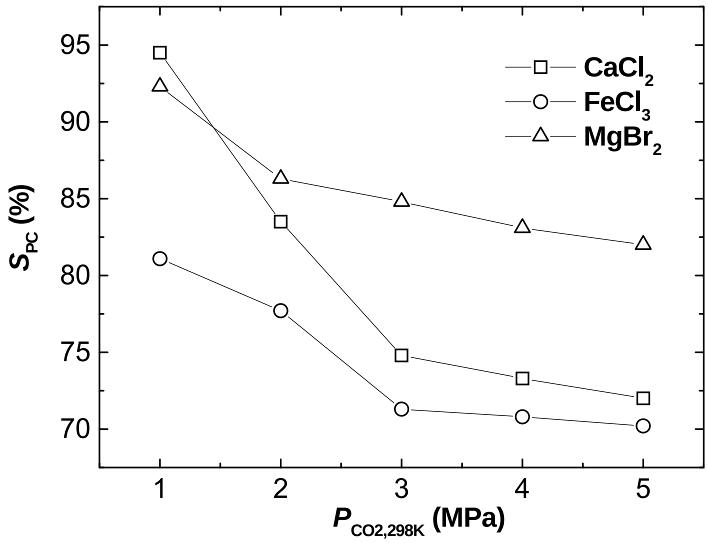



Fig. 5 Effect of initial $CO_2$ pressure ($P_{CO2,298K}$ ) on the selectivity ($S_{PC}$) to propylene carbonate .

The positive effect of low $CO_2$ pressure, above all on the selectivity of PC formation, may be of technical importance. When compared to the contemporary situation, its potential industrial application would not require the material-demanding high-pressure vessels. Of interest is also the low reaction temperature and a potential utilization of partial $CO_2$ pressures to 1 MPa in a continuous process.

With the aim to examine the effects of the lower $CO_2$ pressure and another Lewis base, tributylamine (TBA), we have performed a series of experiments with various epoxy compounds at 120 ± 2°C and different total pressures in autoclave (reaction time 3 h). Similarly to previous cases, also here the autoclave was re-pressurized after the $CO_2$ pressure had significantly decreased in comparison to its initial pressure, at least to 0.8 MPa. Data summarized in Table 6 demonstrate that both with DMF-$CaCl_2$ and the same molar amounts of TBA-$CaCl_2$ the total pressures above 3 MPa decrease the selectivity to cyclic alkylene carbonates, and, as we believe, this also holds for other epoxides. Of worthy of note is also a partial carbon dioxide pressure as a factor that should be taken into account particularly in an addition to low molecular epoxy compounds.

Table 6 Effect of total pressure on the conversion of different epoxy compounds and selectivity of $CO_2$ additions to cyclic carbonates formation at 120 ± 2°C and reaction time 3 h

| Epoxy compound | Total pressure in maintained in autoclave [MPa] | Conversion of epoxy compound [%] | Selectivity to cyclic carbonate [%] |
|---|---|---|---|
| Propylene oxide | 6 – 8 | 100 | 62 |
| Propylene oxide | 2 – 3 | 100 | 92 |
| Propylene oxide | 2 – 3 | 100 | 92 |
| Ethylene oxide | 7 – 9 | 100 | 54 |
| Ethylene oxide | 2 – 3 | 100 | 96 |
| Butylene oxide | 7 – 9 | 100 | 58 |
| Butylene oxide | 1 – 2 | 100 | 92 |
| Butylene oxide[a] | 1 – 2 | 100 | 93 |
| 3,4-epoxy-but-1-ene | 6 – 8 | 100 | 60 |
| 3,4-epoxy-but-1-ene | 1 – 1,8 | 100 | 94 |
| 3,4-epoxy-but-1-ene[a] | 1 – 1,5 | 100 | 95 |
| 1,2-epoxyoctadecane | 6 – 8 | 98 | 58 |
| 1,2-epoxyoctadecane | 0,3 – 0,7 | 94 | 95 |
| Epichlorhydrin | 6 – 8 | 100 | 57 |
| Epichlorhydrin | 1 – 2 | 100 | 89 |
| Glycidyl vinyl ether | 6 – 8 | 97 | 59 |
| Glycidyl vinyl ether | 0,8 – 1,2 | 96 | 91 |
| Glycidyl vinyl ether | 0,7 – 1,1 | 97 | 92 |

*Note: 125 $cm^3$ –autoclave was charged with 258 mmol PO, 205 mmol DMF (TBA) and 7.39 mmol $CaCl_2$ ; 2-6 MPa $CO_2$; [a] TBA as the base*

The results also indicate that as to the mechanism of the addition, the important effect on the insertion of carbon dioxide into the epoxy ring of oxirane and alkyl oxiranes to give alkylene carbonates can be ascribed to the kind of a catalytic system or co-catalyst, that comports with our results and conclusions derived by other authors [42].

We believe that a similar positive effect of the low pressure will be observed also with a combination of other Lewis bases with transition metal, Ca and Mg halides, provided that the reaction medium does not contain water.

In spite of the high PC selectivity achieved in this work with Co, Ni, and Zn halides as cocatalysts of DMF and observed by us also earlier[32], we have paid more attention to Ca halides. We further decided to verify whether reported catalytic behavior of Ni, Co and Fe halides [4,5,32,42] is also maintained under partially changed reaction conditions and to determine the efficiency of Group 2 halides. Last but not least, we attempted at finding a catalyst of choice from technical and economic standpoint that would be safe as far its industrial performance and environmental hazards are concerned.

In the present work we report data of potential industrial interest, paying less attention to detailed discussion of the already reported findings and obvious results.

## 5. Conclusions

We have proved that transition metal halides, especially of Fe triad ($CoCl_2$, $NiCl_2$ and $FeCl_3$) and partially also Group 2 metal halides, particularly $CaCl_2$, $MgCl_2$, $CaBr_2$ and $CaI_2$ are efficient catalysts of DMF and TBA based systems for the addition of $CO_2$ to epoxy compounds to produce the corresponding alkylene carbonates. On the other hand, the corresponding metal carboxylates, nitrates, sulfates and carbonates are practically inactive.

When compared to contemporary technologies, potential industrial use of the systems under conditions reported in this work would not require an expensive high-pressure equipment. Moreover, satisfactory reaction rates and selectivities are obtained with diverse epoxy compounds at 120°C and $CO_2$ pressures below 3 MPa (1 - 3 MPa) , using e.g. DMF and/or DBA – $CaCl_2$ ($CoCl_2$ or $CaBr_2$). In water-free media, the conversion of alkylene oxides is practically quantitative and the selectivity of the addition to alkylene carbonates ranges from 70 to 94 %.

The positive effect of the lower $CO_2$ partial pressure as well as the total pressure in the reaction system has been proved also in the case of other epoxy compounds , leading to a marked increase in the selectivity of their reactions to cyclic alkylene carbonates formation.

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