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Dedicated to professor Gh. Marcu at his 80th anniversary

CATALYTIC SYNTHESIS OF DIMETHYL CARBONATE FROM METHANOL AND CARBON DIOXIDE

JENŐ BÓDIS[1] AND GEORGE A. OLAH[2]

ABSTRACT. The direct synthesis of dimethyl carbonate (DMC) from carbon dioxide and methanol, or dimethyl ether, in presence of magnesium and aluminum methoxide as catalysts was studied. The reactions were performed under batch conditions with catalysts in homogeneous liquid phase of excess methanol (no other solvent was used) at different partial pressures of carbon dioxide and at different temperatures. Depending on the reaction conditions and using magnesium methoxide as catalyst, dimethyl carbonate in 2-7% yield was detected.

Keywords: Dimethyl carbonate; Carbon dioxide activation; Homogeneous catalysis; Magnesium methoxide

INTRODUCTION

The versatile chemical property of dimethyl carbonate (DMC) makes it useful as a phosgene equivalent as well as a methylating and methoxycarbonylating agent [1-3]. On the other hand, replacing hazardous compounds is one of the many goals of environmental chemistry [3].

DMC can also be used as an additive in gasoline to improve fuel combustion and reduce automotive emissions [4]. Formaldehyde emissions were also lower with DMC as octane enhancer than with MTBE.

The industrial synthesis of DMC was based on phosgene [3].

$$ClCOCl + 2\,CH_3OH \rightarrow (CH_3O)_2CO + 2\,HCl$$

In the Enichem synthesis the $CuCl/CuCl_2$ catalyzed oxidative carbonylation reaction of methanol to DMC is used [1,3,4].

$$CH_3OH + 1/2O_2 + CO \rightarrow (CH_3O)_2CO + H_2O$$

Despite the fact that the Enichem process looks very feasible, the reaction is still subject of intensive studies. Kricsfalussy *et. al.* [5] tested molten CuCl-KCl salts as catalysts, Cavinato *et. al.* [6] Pd complexes, and Delledonne *et. al.* [7] Schiff base Co

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[1] "Babes-Bolyai" University, "Babes-Bolyai" University, Department of Organic Chemistry, Arany János 11, 400028 Cluj, Romania,E-mail: jbodis@chem.ubbcluj.ro, Fax: 40-264-590818

[2] Donald P. and Katherine B. Loker Hydrocarbon Research Institute,University of Southern California, Los Angeles, CA 90089-1661, USA

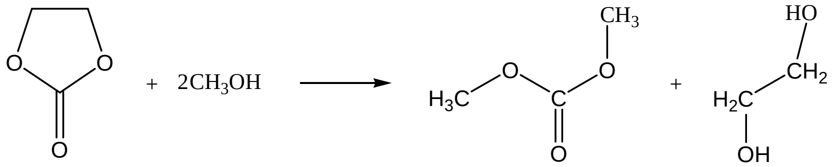
complexes. A Japanese patent [8] reports a complex catalytic system ($PdBr_2$-CuBr-KBr) in the presence of quinones and $KOOCCH_3$, with modest yields at atmospheric pressure. Relatively good space-time yields were obtained by gas phase oxidative carbonylation of methanol over ($PdCl_2$-$CuCl_2$-CH_3COOK)/activated carbon catalytic system [9]. Transition metal (Cu, Pd, Co, Rh) based catalytic systems [10] have been found to catalyze the electrochemical oxidative carbonylation of methanol.

UBE Chemical Industries [1,3,4,11] developed a pilot plant process for DMC production that uses the carbonylation of methyl nitrite over metal halides (Pd+Fe, Cu, Co, Ni or Sn) supported on active carbon.

$$CO + 2\,CH_3ONO \rightarrow (CH_3O)_2CO + 2\,NO$$

$$2\,NO + 2\,CH_3OH + \tfrac{1}{2}\,O_2 \rightarrow 2\,CH_3ONO + H_2O$$

Texaco Chemical [12-14] realized the coproduction of DMC and ethylene glycol through the transesterification of ethylene carbonate with methanol.



Titanium silicate molecular sieve (TS-1), exchanged with an aqueous solution of K_2CO_3 is described to be an excellent catalyst for the above transesterification reaction [15], reaching 57% yield (based on ethylene carbonate) of DMC. Some reports [16-18] claimed that by carrying out the transesterification of alkylene carbonates with methanol in presence of carbon dioxide, part of the methanol was reacting directly with CO_2 to DMC. However, the selectivity was very low and involved significant problems during separation.

The present work focuses on direct synthesis of DMC from carbon dioxide, an environmentally friendly building block, and methanol or dimethyl ether, cheap and available feedstocks of the chemical industry. Both reactions are thermodynamically unfavorable having positive ideal gas phase free energy changes (ΔG) at 100 °C.

$$2\,CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad \Delta G_{100^oC} = +12.2 \text{ kcal/mol}$$

$$CH_3OCH_3 + CO_2 \rightarrow (CH_3O)_2CO \qquad \Delta G_{100^oC} = +15.1 \text{ kcal/mol}$$

There are only few publications dealing with the reaction of carbon dioxide and methanol [19-29], and no literature report was found on the dimethyl ether reaction route. In almost all cases, the reported DMC yields were based on the amount of catalyst used. Using $Bu_2Sn(OCH_3)_2$ as catalyst [19], a 50% DMC yield was reached at 100 °C and 5 bar CO_2 pressure after 24 hours reaction time. In the presence of thallium compounds (ethoxide, or oxide) [20], only low reaction performances were detected (*e.g.* 20 cm^3 CH_3OH resulted only 67-68 mg DMC, corresponding to 0.3% DMC yield based on used methanol). $Bu_2Sn(OBu)_2$-NaBr, $Sn(OBu)_4$-NaBr, and $Ti(OBu)_4$-NaBr systems are described as good catalysts, especially in the presence of dicyclohexylcarbodiimide as water scavenger [21-23] reaching 0.5- 2.68 % DMC yields based on methanol after 20 hours reaction time at

150 ºC and 25-60 bar. Basic catalysts (K_2CO_3, Na_2CO_3, Cs_2CO_3, K_3PO_4, and $(CH_3)_4NOH$) applied together with CH_3I as promoter [24] gave high DMC yield in reactions carried out at 100 ºC and 50 bar CO_2 pressure for 2 hours. Part of the CH_3I promoter is also consumed, making it difficult to evaluate the DMC yield based on the amount of methanol introduced into the reaction mixture. Nevertheless, in the case of K_2CO_3, DMC was obtained even in the absence of CO_2 as reactant.

Without any experimental data regarding the amount of methanol, carbon dioxide, or catalyst used, a short publication [25] claimed 30 % conversion and 99% selectivity after 12 hours reaction time by using *in situ* prepared magnesium methoxide at 180 ºC and at ~15 bar CO_2 pressure.

Results on the use of zirconia (ZrO_2) and zirconia promoted with phosphoric acid as catalysts for direct synthesis of DMC from methanol and CO_2 were also reported [26,27]. The maximum DMC yield (based on methanol) was found to be ~ 0.6% in case of zirconia and around 0.9% in case of promoted ZrO_2 catalysts.

The aim of our present contribution was to find effective catalysts or catalytic systems, and to establish the optimum reaction parameters for the direct conversion of carbon dioxide and methanol to DMC, a high scale required product both as reactant for chemical synthesis, and as gasoline octane enhancing additive.

EXPERIMENTAL

The carboxylation of methanol with carbon dioxide to dimethyl carbonate was carried out in a Parr autoclave (120 cm^3) operated at 10-150 bar and 25 - 180 ºC. Magnetic stirring at a speed of 1100 rpm was used. Weighed amount of catalysts were introduced into the autoclave. After addition of the dry methanol (usually 0.5 - 1.0 mol, Mallinkrodt, AR), the autoclave was sealed, and flushed with nitrogen or helium to remove atmospheric oxygen. The inside temperature was measured by a thermocouple. Carbon dioxide (Air Gas, research grade) was introduced in two different ways:

1.- at room temperature until ~10-55 bar total pressure and the autoclave was then placed in a thermostat bath preset to the reaction temperature.

2. - by adding carbon dioxide only after the catalyst-methanol mixture reached the desired reaction temperature. In this case the reactions had a well-defined starting time.

In the case of *in-situ* prepared methoxide catalysts, both versions were applied, but most experiments were run by introducing carbon dioxide only after the methoxide was prior formed at a higher temperature (1-2 hours at 200-210 ºC for $Mg(OCH_3)_2$ and 220-230 ºC for $Al(OCH_3)_3$). The progress of reaction in time was evaluated from the carbon dioxide consumption (added from a well-known volume reservoir keeping the working pressure in the autoclave constant). After the reaction was terminated, the autoclave was cooled to 0 ºC in a water-ice bath, and the carbon dioxide vented carefully before opening the reaction vessel.

The reactants and products were analyzed using a Hewlett Packard 5971 mass spectrometer and Varian 3300 gas chromatograph equipped with a DB 5, or HP 1 capillary columns and FID detector. When the product mixture appeared as a suspension, filtering was employed before analysis. In most cases of metal methoxide containing mixtures, distillation was applied for the separation of volatile liquid compounds (mostly DMC and methanol) from dissolved catalyst. The water content of the reaction mixture (H_2O formation is supporting the catalytic pathway of the reaction between methanol and CO_2 in presence of methoxide) was analyzed by a gas chromatograph equipped with TCD detector.

RESULTS AND DISCUSSION

The reaction of dimethyl ether with carbon dioxide was checked in different experiments realized at 20 - 180 ºC and 20 - 150 bar with catalysts such as MgO in DMF, $Pd(PPh_3)_4$ in toluene, $Cr(CO)_6$ in pyridine, and magnesium methoxide in methanol. None of these experiments provided positive results. In order to achieve the DMC synthesis from methanol and carbon dioxide, a great number of attempts were carried out at temperatures and pressures mentioned above by testing different catalysts (Et_3N, PPh_3, MgO, $Ru_3(CO)_{12}$, $Pd(PPh_3)_4$, CuPhtc, 5% Rh/C, 10% Pd/C, 5% $Pd/BaCO_3$) and catalytic systems (5% Rh/C + CuCl + KCl, 5% Rh/C + PPh_3 + CH_3I, 5% Rh/C + Et_3N, 5% Rh/C + MgO, 5% Rh/C + Et_3N + CuCl, 5% $Pd/BaCO_3$ + Et_3N, 10% Pd/C + Et_3N). However, the catalysts tested were not able to produce measurable amount of DMC. Tin compounds (SnO_2, $(CH_3)_3SnCl$) were also unsuccessful, as well.

The experimental conditions of our first successful experiments and the results obtained for the conversion of methanol to DMC upon treatment with carbon dioxide are compiled in Table 1. The magnesium methoxide catalysts were prepared *in-situ* from Mg (turnings, Mallinckrodt, AR) and absolute methanol under the depicted reaction conditions, carbon dioxide being present from the beginning. Analyses were done without any preliminary separation by injecting samples in GC, and MS respectively.

Table 1

Reaction conditions and results for the synthesis of DMC from methanol (or dimethyl ether) and carbon dioxide in the presence of magnesium methoxide catalyst prepared *in situ* from Mg and methanol at the reaction conditions.

n_{MeOH} (mol)	n_{MeOMe} (mol)	n_{Mg} (mol)	p_{CO2} (bar)	T_{react} (ºC)	p_{react} (bar)	t_{react} (h)	Y_{DMC}/MeOH (%)	Y_{DMC}/cat (%)
0.50	0.00	0.04	30	170	80	3	1.9	9.7
0.50	0.00	0.04	30	180	130	4	3.2	16.0
0.10	0.10	0.03	35	180	150	5	0.0	0.0

Y_{DMC}/MeOH: yield, molar percentage of methanol converted to DMC.
Y_{DMC}/cat: yield, molar percentage of DMC reported to the amount of catalyst.

As is shown in Table 1, only very low yields of DMC could be detected. By adding dimethyl ether, even the transformation of methanol was blocked.

In the next series of experiments (see Table 2), the magnesium methoxide was prepared in advance by stirring metallic magnesium with methanol at 200 ºC for at least 1 hour, cooling the mixture at the desired reaction temperature, than adding carbon dioxide and running the reaction at constant temperature. Analyses still were done on crude reaction mixtures.

Table 2

Reaction conditions and results for the synthesis of DMC from methanol and carbon dioxide (added only at the desired reaction temperature) in the presence of magnesium methoxide catalyst prepared previously *in-situ* from Mg and methanol at 200 ºC.

n_{MeOH} (mol)	n_{Mg} (mol)	t_{react} (h)	Y_{DMC}/MeOH (%)	Y_{DMC}/cat (%)
0.50	0.05	5	1.9	7.5
0.50	0.04	12	4.3	22.6
0.50	0.04	12	4.6	24.0

p_{CO2}= 25 bar; T_{react} = 177 ºC; p_{react} = 55 bar
Y_{DMC}/MeOH: yield, molar percentage of methanol converted to DMC.
Y_{DMC}/cat: yield, molar percentage of DMC reported to the amount of catalyst.

As shown in Table 2, the preformed catalyst led to a small increase of DMC yields, about 1%. The increased amount of magnesium didn't have a benefic effect on the reaction as part of the magnesium was found untransformed in the crude product mixture. Of course, the lower reaction time can be also a reason for the lower yield, as well.

In order to eliminate the analyses difficulties (needle blocking, reactions induced by the methoxide in the GC injector), the resulted reaction mixtures of the next experiments were separated by distillation before analysis. The yields included in Table 3 are dependent on reaction temperatures and pressures.

Table 3

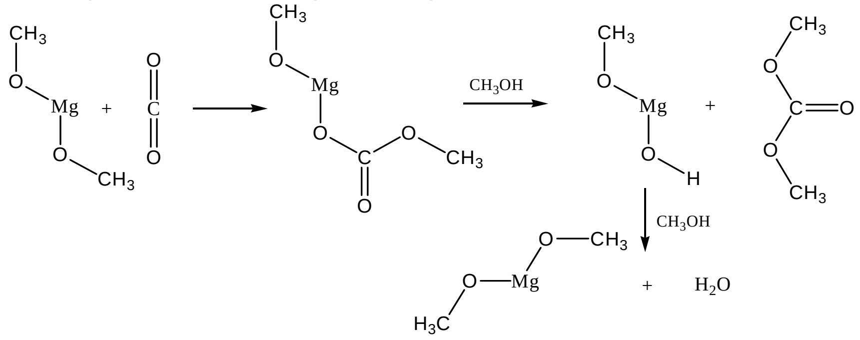
Reaction conditions and results for the synthesis of DMC from methanol and carbon dioxide (12 hrs reaction time) catalyzed by magnesium methoxide preformed *in-situ* from Mg and methanol at 200 C. Carbon dioxide (p_{CO2} = 50 bar) was added to the CH_3OH-$Mg(OCH_3)_2$ mixtures at 50 ºC.

Entry	n_{MeOH} (mol)	n_{Mg} (mol)	T_{react} (ºC)	p_{react} (bar)	Y_{DMC}/MeOH (%)	Y_{DMC}/cat (%)
1	0.50	0.04	50	50	0.0	0.0
2	0.50	0.04	100	67	0.0	0.0
3	0.50	0.04	150	85	2.7	14.4
4	0.50	0.04	160	92	5.0	26.2
5	0.50	0.04	170	98	6.7	35.3
6	0.50	0.04	180	106	7.2	37.6
7*	0.50	0.04	180	140	5.5	28.2
8	1.00	0.08	170	103	6.8	35.8
9	0.50	0.02	170	103	3.7	42.9

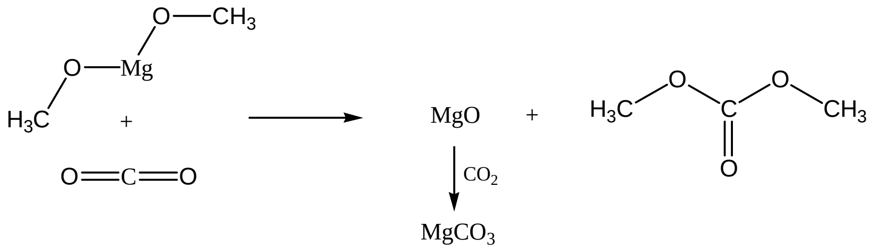
Y_{DMC}/MeOH: yield, molar percentage of methanol converted to DMC.
Y_{DMC}/cat: yield, molar percentage of DMC reported to the amount of catalyst.
*added 50 bar CO_2 at 25 ºC.

At low temperatures (50-100 ºC), the reaction practically did not work. Increase in temperature had a positive effect on the DMC yield, the maximum yield being detected at 180 ºC. However, the variation of yields had a higher slope in the range of 150 - 170 ºC than in the temperature range of 170 - 180 ºC. The problem encountered with these experiments was, that by going up with temperature, the partial pressures of methanol and especially CO_2, are rising up. Therefore, the positive effect on the DMC yield must be attributed to both parameters, temperature and pressure together. The diminished yields obtained at high partial pressures of carbon dioxide (140 bar total pressure, Entry 7), indicates that at a certain value of the CO_2 pressure, the catalyst can be carbonated, losing its activity. A decreased amount of catalyst is leading to lower DMC yield, but to a higher catalyst related yield (Entry 9).

The content of water was measured by GC-MS analysis in the product mixture (Entry 6) and it was found to be 056 mol/l water, lower than the concentration of DMC (0.88 mol/l). It appeared to us that part of water reacts with magnesium methoxide forming CH_3OH and $Mg(OH)_2$ and deactivating the catalyst. Nevertheless, the presence of water in the product mixture is supporting our initial assumption that the reaction should be catalytic and DMC was mainly formed by insertion of CO_2 in magnesium methoxide. The resulting adduct reacts with methanol leading DMC, water and the reformed magnesium methoxide (Scheme 1).



Scheme 1. Catalytic pathways during the formation of DMC from carbon dioxide and methanol in presence of magnesium methoxide.



Scheme 2. Possible non-catalytic route for the formation of DMC through nonreversible reaction of magnesium methoxide with excess carbon dioxide.

However, at higher CO_2 pressures and higher temperatures (Entry 7), can be supposed another reaction route involving the $Mg(OCH_3)_2$ catalyst and CO_2, yielding DMC and $MgCO_3$ (Scheme 2). This reaction is also deactivating the catalyst and should be avoided during the DMC synthesis.

The upcoming experiments were done at different temperatures by using also preformed methoxide catalysts. CO_2 was introduced only when the methanol-magnesium methoxide mixture reached the desired reaction temperature. The reaction conditions and the obtained yields are given in Table 4.

Table 4

Reaction conditions and results for the synthesis of DMC from methanol and carbon dioxide (12 hrs reaction time) catalyzed by magnesium methoxide preformed *in-situ* from Mg or Al and methanol at 200 ºC and220 ºC respectively. Carbon dioxide (p_{CO2} = 20-25 bar) was added to the CH_3OH-methoxide mixtures only when the desired reaction temperature has been reached.

Entry	n_{MeOH} (mol)	n_M (mol)	T_{react} (ºC)	p_{react} (bar)	Y_{DMC}/MeOH (%)	Y_{DMC}/cat (%)
1	0.50	0.04	180	60	4.3	22.6
2	0.50	0.04	170	55	3.8	19.7
3	0.50	0.04	160	55	3.6	18.7
4	0.50	0.04	150	55	2.8	14.5
5*	0.50	0.04	170	55	0.4	1.7
6**	0.50	0.05	170	55	0.2	0.4

Y_{DMC}/MeOH: yield, molar percentage of methanol converted to DMC.
Y_{DMC}/cat: yield, molar percentage of DMC reported to the amount of catalyst.
*4 Å molecular sieve (Mallinckrodt) as water scavenger.
** Al as catalyst precursor.

Aluminum methoxide has also shown some activity (Entry 6). Although seen as a promising option, was not further explored in this study.

The use of a molecular sieve as water scavenger (Entry 5) had a negative effect on the reaction. Our finding is different from the almost neutral influence found for a 3Å molecular sieve on DMC formation over ZrO_2 catalyst [26], or from the positive effect of a 4Å molecular sieve revealed in case of DMC synthesis from methanol, carbon dioxide and methyl iodide mixture in presence of K_2CO_3 as catalyst [29].

At almost constant carbon dioxide partial pressures, an increase of temperature slowly increased the yields in the temperature range of 150-180 ºC (see Figure 1).

A few experiments of DMC synthesis were also realized by operating the batch pressure reactor in a continuous mode. Thus, with the help of a dip tube, a constant CO_2 flow was passed through the methoxide-methanol mixture keeping the pressure at 40–50 bar inside the autoclave, and continuously venting CO_2, DMC, CH_3OH, and water. Having the amount of distillate/time and the DMC content of the flux, we were able to evaluate the rate of DMC formation (turnover frequency, TOF = 0.08 - 0.1 $mol_{DMC}/mol_{Mg}.h$).

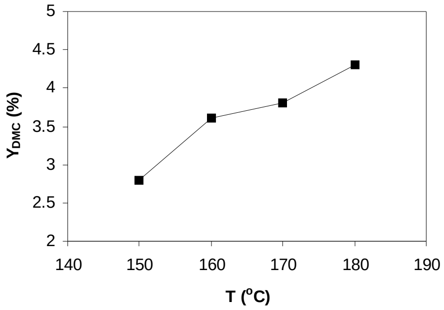


Figure 1. Effect of reaction temperature on the DMC yields under the conditions given in Table 4.

CONCLUSIONS

Magnesium methoxide looks to be a promising catalyst for the direct synthesis of dimethyl carbonate from carbon dioxide and methanol. Since the reaction can be performed in excess of methanol, there is no need for another organic solvent as reaction medium.

The catalyst is deactivated by water (a green byproduct of the reaction) and by high carbon dioxide partial pressures. Continuous operation of the process in both, homogeneous or heterogeneous reaction at optimum pressures and temperatures will be able to diminish this inconvenience in the near future.

Dimethyl ether could not be converted to dimethyl carbonate through direct reaction with carbon dioxide under the conditions investigated in this study.

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