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Preliminary Communication

Oxidative carbonylation of methanol to dimethyl carbonate (DMC): a new catalytic system [☆]

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Abstract

Oxidative carbonylation of methanol to dimethylcarbonate catalysed by cobalt complexes is reported. Cobalt complexes with oxygen and or nitrogen donor ligands such as carboxylate, acetylacetonate, picolinate and Schiff bases are suitable catalysts. The oxidative carbonylation of methanol catalysed by cobalt complexes which has never been reported, affords dimethylcarbonate with remarkably high selectivities. Of the cobalt complexes, those with Schiff bases show the highest reactivity. The influence of co-solvents was also examined.

Keywords: Cobalt; Carbonylation; Methanol; Catalysis; Dimethyl carbonate

1. Introduction

Non-toxic, non-polluting dimethylcarbonate (DMC) is achieving increasing importance as a versatile intermediate and product. DMC could replace methylating agents such as dimethyl sulphate and methyl halides, or carbomethoxylating and carbonylating systems in industrial applications [1].

DMC is also being considered as a component of reformulated fuels, owing to its high oxygen content and good blending properties [2]. For these reasons industrially viable dimethylcarbonate preparations are attracting more and more interest. Industrially DMC and, generally, the carbonic acid esters are synthesised by reaction of the corresponding alcohols with phosgene [3] according to the reaction (see Eq. (1)).

$$2ROH + COCl_2 \longrightarrow CO(OR)_2 + 2HCl \qquad (1)$$

In the early 1980s an alternative technology was developed for industrial syntheses of DMC based on the oxidative carbonylation of methanol in the presence of cuprous chloride according to the reaction (Eq. (2)) [4].

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

Other than copper-based systems a few catalytic systems are able to catalyse the oxidative carbonylation of methanol to DMC in the liquid phase including systems based on palladium [5], selenium [6], or bromine [7].

2. Results and discussion

We found that cobalt-based systems are able to catalyse oxidative carbonylation of methanol to DMC. Cobalt(II) complexes bearing ligands with nitrogen and oxygen donors such as carboxylate, acetylacetonate, Schiff bases and picolinate produce DMC with high selectivity in methanol under carbon monoxide and dioxygen mixtures. These catalytic cobalt systems appear very attractive as they are non-corrosive and produce DMC with remarkable selectivity and reaction rate.

In Table 1 we report the data obtained by reaction of methanol to form dimethylcarbonate under carbon monoxide and dioxygen in the presence of cobalt com-

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Table 1
Dimethylcarbonate formation by cobalt complexes

Catalysts (mol/l)	Time h	Temperature °C	Conversion [c] %	Selectivity [c] %	DMC [a] g	Turnover number
$[Co(CH_3COO)_2(H_2O)_4]$ (0.16)	1.16	130	4	90	2.5	2.8
$[Co(acac)_2]$ (0.16)	3.25	105	3.8	92	2.5	2.8
$[Co(acac)_2(bipy)]$ (0.08)	5	100	6.5	98.5	4.5	10
$[Co(acac)_3]$ (0.16)	2	105	2	50 [b]	1.5	1.6
Co(*iso*-butyrate)$_2$ (0.16)	4	120	2.6	98	1.8	2
$Na[Co(acac)_3]$ (0.16)	1.5	100	3.5	96	2.4	2.6
$[\{Co(salen)\}_2]\cdot H_2O$ (0.08)	1	120	18.1	98	12.5	13.8 [d]
$CoCl_2$ (0.16)	5	120	–	–	–	–

[a] g.l.c. yields.
[b] The major product was formaldehyde dimethyl acetal.
[c] Based on methanol.
[d] Based on cobalt. (acac) = acetylacetonate; (bipy) = bipyridyl; H_2salen = 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene. Experimental conditions: pressure 30 kg cm^{-2} initial, carbon monoxide: dioxygen ratio 2:1; methanol 50 g.

plexes. Simple $CoCl_2$ is inactive as catalyst and when we used $[Co(acac)_3]$ the major product was not DMC but formaldehyde dimethylacetal, produced by oxidation of methanol. The best results for DMC productivity and turnover number were obtained with $[\{Co(salen)\}_2]\cdot H_2O$. For this reason we synthesised other Schiff bases cobalt(II) complexes, and we obtained the data in Table 2, with methanol conversion range of 10–30% and selectivity range of 96–99%. These experiments were run at constant pressure by feeding in carbon monoxide and dioxygen continuously.

The major by-product was carbon dioxide, its selectivity based on total carbon monoxide being in the range of 30–50%. Cobalt Schiff base complexes appeared to be very attractive catalysts but under the reaction conditions ligand oxidative degradation occurred [8] and the reaction rate decreased. In stopping the reaction before complete ligand degradation, we could isolate cobalt(III) species. For example, when we

Table 2
Shiff base cobalt complexes catalysed formation of dimethylcarbonate

Catalyst (mol/l)	Time, h	Conversion [d] %	Selectivity [d] %	DMC [a] g	Turnover number
$[\{Co(salen)\}_2]H_2O$ (0.008)	5	9.1	99	15.1	71 [b]
$[\{Co(salen)\}_2]H_2O$ (0.015)	7	20	99	32	79 [b]
$[\{Co(salen)\}_2]H_2O$ (0.029)	7	27	99	45.2	54 [b]
$[Co(Mesalen)(H_2O)]$ (0.063)	5	12	98.6	20.2	24 [b]
$[Co(5\text{-}MeOsalen)(H_2O)]$ (0.054)	6	16	99	33.6	35 [c]
$[Co(Naftsalen)(H_2O)]$ (0.054)	5.5	1.2	96.5	2.5	3 [c]
$[Co(4,6\text{-}diMeOsalen)(H_2O)]$ (0.041)	6	6	98	13.1	17 [c]

[a] g.l.c. yield.
[b] Methanol 150 ml.
[c] Methanol 200 ml.
[d] Based on methanol. H_2Mesalen = 2,7-bis(2-hydroxyphenyl)-3,6-diaza-2,6-octadiene; H_2 5 MeOsalen = 1,6 bis(2-hydroxy-5-methoxyphenyl)-2,5-diaza-1,5-hexadiene; 4,5-diMeOsalen = 1,6 bis(2-hydroxy-4,6-dimethoxyphenyl)-2,5-diaza-1,5-hexadiene; H_2 Naphsalen = 1,6 bis(2-hydroxynaphthyl)-2,5-diaza-1,5-hexadiene. Experimental conditions: 120°C; 20 kg cm^{-2} carbon monoxide: dioxygen ratio 4:1.

used $[\{Co(salen)\}_2]\cdot H_2O$ we observed $[Co(salen)COOCH_3(H_2O)]$ identified by its $\nu(CO)$ band at 1673 cm^{-1} [9]. This cobalt(III) complex is a true catalyst precursor, and when we used it we obtained the same reaction rate as with $[\{Co(salen)\}_2]\cdot H_2O$.

We tested the reactivity of $[Co(salen)COOCH_3(H_2O)]$ in methanol, ethanol, and toluene under dinitrogen at 100°C in the following reactions:

$$2[Co(salen)COOCH_3(H_2O)] \xrightarrow[\text{methanol}]{N_2 100°C} [\{Co(salen)\}_2]L + CH_3OCOOCH_3 + CO \quad (3)$$

$$2[Co(salen)COOCH_3(H_2O)] \xrightarrow[\text{ethanol}]{N_2 100°C} [\{Co(salen)\}_2]L + CH_3CH_2OCOOCH_3 + CO + CH_3OH \quad (4)$$

$$[Co(salen)COOCH_3(H_2O)] \xrightarrow[\text{toluene}]{N_2 100°C} \text{no reaction} \quad (5)$$

With methanol we found that DMC was produced in yields of ca. 0.5 mol per mol of $[Co(salen)COOCH_3(H_2O)]$, and that carbon monoxide was evolved. On carrying out the reaction in the presence of ethanol, ethyl methyl carbonate was produced in about 0.4 mol per mol $[Co(salen)COOCH_3(H_2O)]$ and no DMC was detected, carbon monoxide was also evolved in the reaction. At the same temperature under dinitrogen, in toluene, we found that almost no reaction occurred and we detected only traces of carbon monoxide.

From these observations we presume that DMC and $CH_3CH_2OCOOCH_3$ formation in reactions (3) and (4) comes from nucleophilic attack of an alcohol molecule on the carbomethoxy moiety [5], with formation of a cobalt(I) hydride that is oxidised to cobalt(II) species by action of a cobalt(III) complex, as described in Ref. [10].

In Fig. 1 is depicted a possible reaction pathway that takes account of the previous observations. Initially oxidation of $[\{Co(salen)\}_2]\cdot(H_2O)$ in the presence of methanol gives $[Co(salen)OCH_3]$ that under carbon monoxide produces complex $[Co(salen)COOCH_3]$. This complex, with the assistance of a Co^{III} species, can react with a molecule of methanol affording DMC and regenerating $[\{Co(salen)\}_2]$. Formation of carbon dioxide, the major by-product, can be accounted for by a similar pathway involving [Co(salen)OH], which is formed in the presence of water.

Oxidative degradation of the salen stops the catalytic cycle and causes by-product formation.

With the aim of stabilising the catalytic system we looked for ligands more able than Schiff bases to withstand oxidative degradation. Pyridine-2-carboxylates (pic) are known to be stable under oxidative conditions at room temperature and are used in olefin epoxidation with peroxide [11] and benzene hydroxylation [12] with vanadium complex catalysts. We used a cobalt(II) picolinate complex as catalyst for oxidative carbonylation of methanol to DMC. In Table 3 we report the data obtained.

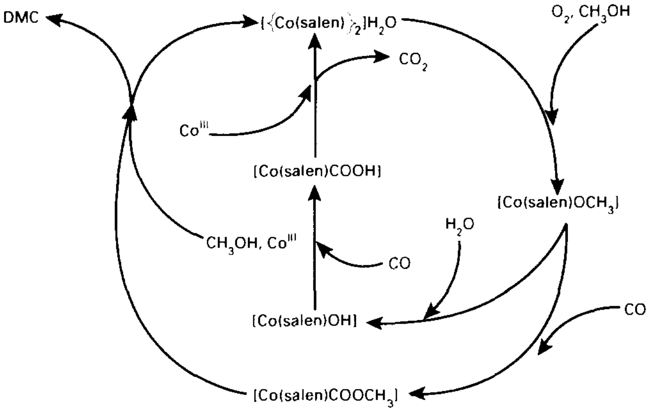

Fig. 1. Mechanism of Cobalt Schiff-base catalysed oxidative carbonylation of methanol to dimethylcarbonate.

After eleven runs no significant decrease of activity was observed [13]. $[Co(pic)_2(H_2O)_4]$ showed high selectivity towards DMC formation (about 98%) with a conversion of methanol of about 10% at 120°C, that increased to 15–16% at 130°C. In comparison with Schiff-base complexes of cobalt, $[Co(pic)_2(H_2O)_4]$ is less active but it maintains its activity longer. During our 100 h test we observed a slow decrease of activity and we isolated an insoluble and inactive species from the reactor, the purple complex $[Co(pic)_3]$ [14]. With the aim of increasing the stability and reactivity of $[Co(pic)_2(H_2O)_4]$ we introduced a coordinating co-

Table 3
$Co(pic)_2\ 4H_2O$ catalysed dimethylcarbonate formation

Run No	Temperature °C	Conversion [c] %	Selectivity [c] %	DMC [a] g	Turnover number
1	120	7	98.5	15.6	13.4
2	120	9.5	98.5	20.7	18
3	120	7.3	99.5	16.2	16
4	120	10.3	99.2	22.7	23
5	120	9.7	99.2	21.6	22
6	120	9.9	99.2	21.7	22
7	120	9.6	98.8	21	21
8	120	9.8	99	21.6	22
9	130	12.5	99	27.4	27
10	130	13.8	98.2	30.2	30
11 [b]	130	16.2	96.3	35.6	36
			Total Turnover number		250.4

[a] g.l.c. yield.
[b] reaction time 8 h.
[c] Based on methanol. pic = pyridine-2-carboxylate. Catalyst $[Co(pic)_2(H_2O)_4]$ (0.065 mol/l), methanol 200 ml, 20 kg cm^{-2} with carbon monoxide: dioxygen ratio 4:1, reaction time 5 h.

Table 4
Co-solvent effect on methanol oxidative carbonylation catalysed by $[Co(pic)_2(H_2O)_4]$

Co-solvent	Conversion [b] %	Selectivity [b] %	DMC [a] g	Turnover number
–	5.6	98.5	6.1	7
$HCON(CH_3)_2$	6.9	99	7.5	9.5
$CH_3CON(CH_3)_2$	7.7	97	8.2	9
$[(CH_3)_2N]_2CO$	8.1	97	8.7	10
C_6H_5CN	6.6	96	7	8
CH_3CN	7.4	93	7.6	8.5
$(CH_3)_2SO$	8.7	94	9.1	10
N-methylpyrrolidone	6.1	96	6.5	7
$(C_6H_5O)_3PO$	0.5	–	0.6	–

[a] g.l.c. yield.

[b] Based on methanol. Catalyst $[Co(pic)_2(H_2O)_4]$ 0.1 mol/l, co-solvent 0.76 mol/l, methanol 100 ml, 30 kg cm^{-2} with carbon monoxide: dioxygen ratio 2:1, 130°C, reaction time 1.5 h.

solvent into the reaction system [15] (Table 4) *N*,*N*-disubstituted amides, aromatic and aliphatic nitriles, tetra-substituted ureas, and sulfoxides increased DMC yield and turnover number. On the contrary triphenyl phosphate prevented DMC formation. In a continuous run of 100 h (145°C, 40 kg cm^{-2} pressure with carbon monoxide oxygen molar ratio (100:3) and $[Co(pic)_2(H_2O)_4]$ (0.024 mol) we determined a turnover number of 157. Under similar conditions, but with *N*,*N*-dimethylacetamide (0.13 mol), we measured a turnover number of 247 without any decrease of activity. A mechanism similar to that shown for $[\{Co(salen)\}_2] \cdot H_2O$ may be also involved in the case of $[Co(pic)_2(H_2O)_4]$ but we have not isolated any intermediate species. The co-solvent effect is still to be explained.

3. Experimental details

The cobalt complexes used in the experimental tests were prepared according to literature methods $[Co(acac)_2(H_2O)_2]$ [16], $[Co(acac)_2(bipy)]$ [17], $[Co(acac)_3]$ [18], $Na[Co(acac)_3]$ [19], $[\{Co(salen)\}_2]H_2O$ [20], $Co(Mesalen)H_2O$, $Co(5\text{-}MeOsalen)H_2O$ and $[Co(pic)_2(H_2O)_4]$ [21], while $[Co(Naphsalen)(H_2O)]$ and $[Co(4,6\text{-}diMeOsalen)(H_2O)]$, were prepared by a method similar to that reported by Bailes [21]. Other cobalt catalysts were purchased from Aldrich Chemicals or Strem Chemicals Inc. Methanol and co-solvents were used as received without any purification and were analysis grade. Carbon monoxide and dioxygen purity were higher that 99%.

3.1. Oxidative carbonylation of methanol

Experiments were carried out in a stainless steel autoclave of 0.250 or 0.500 l of capacity, provided with a magnetic stirrer. Methanol and cobalt complexes were charged in the amounts shown in Tables 1, 2, 3 and 4, and pressurized at room temperature with carbon monoxide and then with dioxygen to the pressures in the Tables. Then heating was started. In the experiments listed in Tables 2 and 3, gases were fed continuously to the autoclave and measured with a mass flow meter, part were leaked at constant pressure, measured and analysed by g.l.c.

In the experiments reported in Table 3 the catalyst was recovered by liquid evaporation after 5 h, fresh methanol was loaded, and the catalyst used again. This operation was repeated eleven times.

3.2. [Co(salen)COOCH$_3$(H$_2$O)]reactivity

The cobalt complex was synthesised according to [9]. Experiments were carried out in a stainless steel autoclave of 0.25 l of capacity, provided with a magnetic stirrer. $[Co(salen)COOCH_3(H_2O)]$ (4.06 g 10 mmol) was loaded into the autoclave and 50 g of methanol (or ethanol or toluene) were added. The air was purged, the autoclave was pressurized with dinitrogen to 5 kg cm^{-2}, and then heating was started. After five h at 100°C the reaction was cooled, and gases and liquids analysed by g.l.c.

Gas chromatographic (g.l.c.) analyses were performed on 25 m Porapak Q column and gas g.l.c. analyses were performed on Carbosieve S-II column.

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