

ACTIVATION OF CH₃OH AND CO₂ BY METALLOPHTHALOCYANINE COMPLEXES: POTENTIAL ROUTE TO DIMETHYL CARBONATE

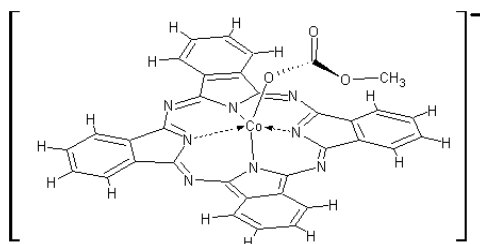
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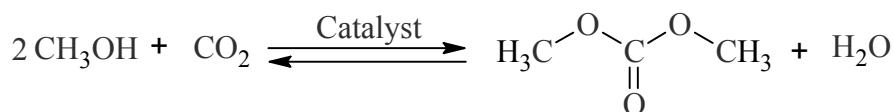
In this present work, the ability of metallophthalocyanines MnPc, FePc and CoPc to activate carbon dioxide and methanol was investigated by FTIR spectroscopy. The formation of a hemicarbonate moiety bonded to the central metal of the MPC was highlighted under mild (bubbling CO₂, 20°C) as well as more drastic conditions (30 bar CO₂, 140°C). Analysis by gas chromatography of the organic phase recovered after bubbling CO₂ showed the presence of DMC.



INTRODUCTION

Dimethyl carbonate (DMC) is a green reagent¹ which has various applications in the pharmaceutical² and polymer³ industries. Unfortunately, its production involves hazardous processes for environment and worker safety (EniChem, UBE and transesterification processes). In the recent years, great efforts have been developed to propose new routes for the synthesis of DMC.⁴ The use of carbon dioxide and methanol (Scheme 1) is one of the most attractive for this purpose. Indeed, CO₂ is a key molecule, a

greenhouse gas and a non-toxic, inexpensive and abundant reagent. However, regarding its chemical inertness, great effort is needed to develop efficient homogeneous or heterogeneous catalytic systems in order to promote the reaction. Many catalytic systems have been tested including acid-base metal oxides,⁵ and transition metal complexes.^{6,7,8} For all systems, yields towards DMC were shown to be low, due to the thermodynamic limitation of the reaction. Therefore, the direct synthesis of DMC from methanol and carbon dioxide is still at a laboratory scale stage.



Scheme 1 – Direct synthesis of dimethyl carbonate from methanol and CO₂.

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Metallophthalocyanine complexes (MPc) have been successfully used for the synthesis of propylene carbonate from propylene oxide and carbon dioxide.^{9,10} For example, Texaco Chemical reached a yield of 76% in propylene carbonate with chromium phthalocyanine.¹¹ However, to our knowledge no example has been published on the use of MPcs to catalyze the formation of DMC from methanol and CO₂.

RESULTS AND DISCUSSION

In our present report, we investigate the reactivity of commercially available metallophthalocyanines against carbon dioxide and methanol by FTIR spectroscopy. The study was first performed under mild conditions. The results were later confirmed under pressurized CO₂ and high temperature. These conditions were tested because this equilibrated reaction is favored by high CO₂ concentration and kinetically enhanced by temperature.

Fig. 1 shows the spectra of the solid obtained for tests using CoPc. After bubbling CO₂, new bands appeared. This clearly demonstrates that reaction between CO₂, methanol and CoPc occurred. The strong absorption at 1727 cm⁻¹ indicates the presence of carbonyl specie. This value is in agreement with those (1720 cm⁻¹) observed by Kasuga *et al.*¹² when bubbling carbon dioxide into a chloroform solution of tetra-*t*-butylphthalocyaninatoaluminum(III)ethoxide and 1-methylimidazole. The authors concluded that

carbon dioxide was inserted between aluminum and ethoxy group to form an Al-O-(CO)-O-CH₂CH₃ moiety. In our case, the additional strong band at 1286 cm⁻¹ is attributed to $\nu_{\text{sym}}(\text{C}(\text{O})-\text{O})$. These two CO stretching bands separated by $\Delta\nu = 441 \text{ cm}^{-1}$ confirm the formation of the hemicarboxylate moiety $\eta^1\text{-O}$ -coordinated to cobalt as indicated in Scheme 2. Indeed, the degree of the separation between the two CO stretching bands differs depending on the coordination mode of CH₃OCO₂⁻ ion.¹³ Compared to the free ion for which $\Delta\nu = 330 \text{ cm}^{-1}$, the degree of separation is larger in unidentate coordination and smaller in bidentate coordination. For example, the reaction of Nb(OMe)₅ with CO₂ in methanol gives a $\eta^2\text{-O}_2\text{O}$ -hemicarboxylate Nb complex¹⁴ with $\Delta\nu = 270 \text{ cm}^{-1}$.

The methoxy group is highlighted by the presence of C-H and C-O vibrations. The intense bands located at 2961 and 2874 cm⁻¹ are characteristic of a methyl group. They correspond respectively to C-H antisymmetric and symmetric stretching vibrations. The additional band at 2934 cm⁻¹ usually attributed to a methylene group can also be ascribed to a methyl vibration with a lowering of symmetry.¹⁵ An interaction between the methyl group and the phthalocyanine ligand inducing a lowering symmetry from C_{3v} to C_s can be suggested. In addition, two new bands which appear at 1443 and 1384 cm⁻¹ are attributed to C-H bending vibrations. The $\nu(\text{C}-\text{O})$ of the methoxy group is classically observed around 1070 cm⁻¹.

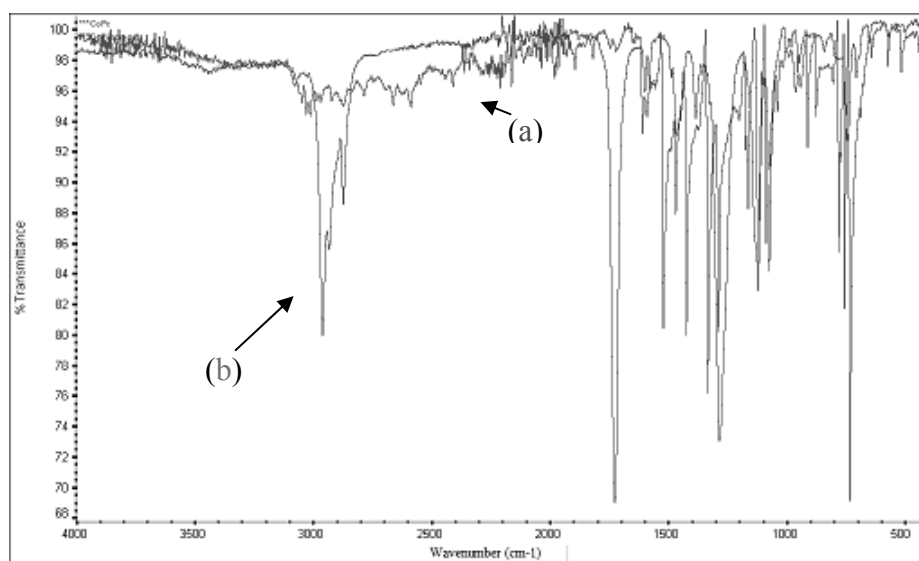


Fig. 1 – FTIR absorption changes of CoPc upon addition of CO₂ at atmospheric pressure and room temperature; (a) CoPc ; (b) CoPc after addition of CO₂.

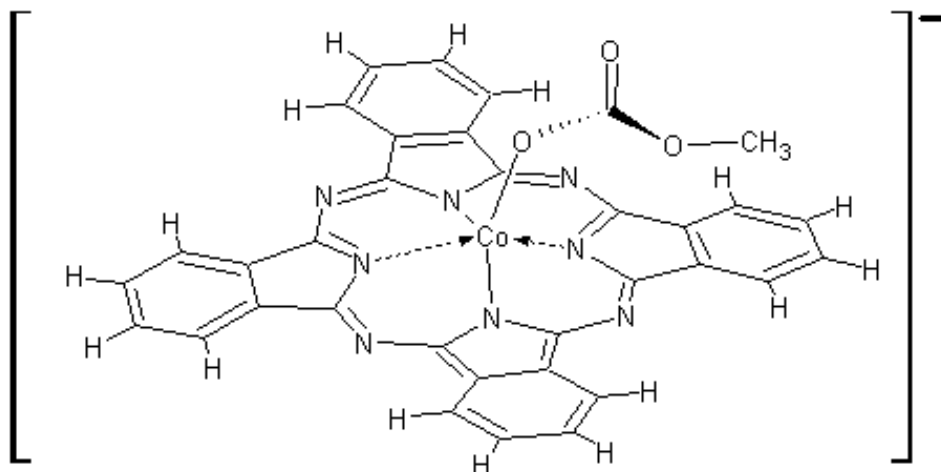
Scheme 2 – Hemicarbonate Moiety η^1 -O-coordinated to cobalt phthalocyanine.

Table 1

For MPc and MPc adducts, wavenumbers of CO vibrations and M-N band versus Metal

MPc	CO Bands after reaction with CO ₂ and methanol			M-N Band	
				Before reaction with CO ₂	After reaction with CO ₂
	$\nu(\text{CO})$ (cm ⁻¹)	$\nu(\text{O}(\text{CO})\text{O})$ (cm ⁻¹)	$\Delta\nu^*$ (cm ⁻¹)	$\nu(\text{M-N})$ (cm ⁻¹)	$\nu(\text{M-N})$ (cm ⁻¹)
MnPc	1721	1275	446	903	1037
FePc	1728	1288	440	909	1039
CoPc	1727	1286	441	913	1039

*: $\Delta\nu = \nu(\text{CO}) - \nu(\text{O}(\text{CO})\text{O})$

A band was effectively observed at 1075 cm⁻¹, but the presence in this region of C-N stretching and C-H in-plane bending vibrations of phthalocyanine rings induces difficulties to propose unambiguous attribution. Moreover, the medium intensity Metal-Nitrogen (M-N) band which is present in the range 903-913 cm⁻¹ for each MPc^{16,17} was shifted to higher wavenumbers after bubbling CO₂ (Table 1). This is further evidence that the reaction has taken place.

Additional analysis of the organic liquid filtrate by GC / FID, after exposure to CO₂, showed the presence of traces of DMC (about 5 ppm). This is further evidence of the reactivity of metallophthalocyanines towards carbon dioxide

and methanol. In this experimental case, the hemicarbonate species displayed above reacts with a second methanol molecule to produce DMC.¹⁸

Similar results were obtained when the reaction was performed under 30 bars of CO₂ and at 140°C. Fig. 2 shows the evolution of both CO vibrations (1724 and 1291 cm⁻¹) over time for CoPc. The differences observed between Table 1 and Fig. 2 for CO vibration wavenumbers are attributable to solvation phenomena for the hemicarbonates in high pressure runs. The GC-FID analysis of similar media showed DMC quantities of approximately 15 ppm. The CO₂ excess in the experiment brings about disequilibrium of reaction, and improves moderately the yield.

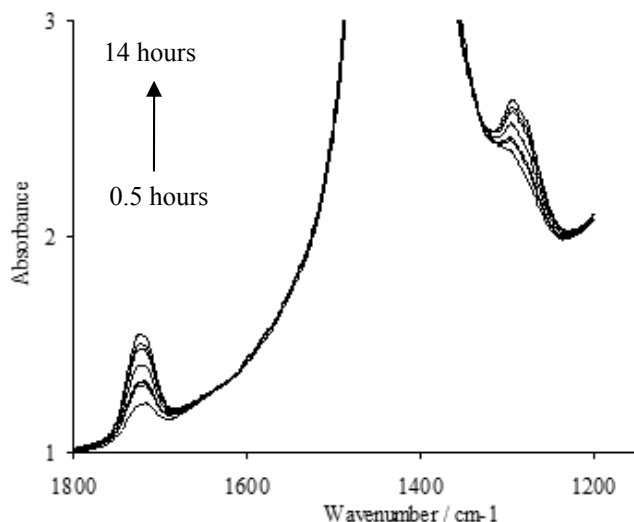


Fig. 2 – In-situ FTIR absorbance of reaction media over time (0.5-14 hours).

EXPERIMENTAL

All solvents and chemicals used were of analytical grade and were used without further purification. CoPc, FePc and MnPc were supplied by Europhthal (France). Methanol 99.8% (GC grade, H₂O < 0.02%) and liquid carbon dioxide (H₂O content < 7 ppm) were delivered from Panreac and Air Liquide respectively.

Atmospheric pressure and room temperature tests

Carbon dioxide was bubbled into 50 mL of methanol, while 1 mmol of metallophthalocyanine MPc (M = Mn, Fe, Co) was slowly added under magnetic stirring. Bubbling CO₂ was maintained for 4 hours. Then, the system was left stirring under CO₂ overnight. The mixture was filtered. The filtrate was concentrated to dryness under a CO₂ stream before FTIR analysis using the BX II Perkin Elmer spectrometer.

High pressure tests

The experiments were performed under 30 bars of CO₂ and at 140°C. For this study, MPc (0.01 mmol) in 1 mL of methanol was introduced into a high pressure cell equipped with quartz windows using a path length of 2.5 cm (set-up described elsewhere¹⁹). The cell was heated and then carbon dioxide was inserted into the cell with a high-pressure pump. The reaction conditions were chosen in order to ensure a diphasic system where the complex is, as much as possible, solubilized in the methanol rich liquid phase for better observation. The reaction was monitored during 14 hours by infrared spectroscopy using a Bio-rad (FTS-60A) spectrometer.

Chromatographic conditions

The organic filtrates were analyzed with a GC Ultra Trace Thermoscientific equipped by a FID detector and a Restek 502.2 polar column (30 m, 0.25 mm, 1.4 μm). The GC conditions were: He carrier (1.6 mL.min⁻¹; split ratio 40), T_{injector} = 250°C; T_{oven} = 50°C then increasing 10°C/min to 150°C; T_{FID} = 250°C; V_{injection} = 1 μL. In our experimental conditions, the LOD (limit operating detection) was evaluated to 1 ppm. For 5 repeats at 5 ppm, the RSD (residual standard deviation) was 12%.

CONCLUSIONS

Commercial metallophthalocyanine complexes (M = Mn, Fe or Co) are able to activate carbon dioxide and could be adequate candidates for the direct synthesis of DMC from methanol and CO₂. Further experiments are now in progress in order to improve the product yields and to get more information about the reaction route. Especially, the influence of temperature and pressure upon this equilibrated reaction will be studied. It could be also interesting to evaluate the amount of soluble species.

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