

# THE ROLE OF SUPERCRITICAL CARBON DIOXIDE IN THE SYNTHESIS OF ORGANIC CARBONATES

Danielle Ballivet-Tkatchenko\*<sup>a</sup>, Stéphane Chambrey,<sup>a</sup> Helka Turunen<sup>b</sup> and Riitta Keiski<sup>b</sup>

<sup>a</sup> LSEO, UMR 5188 CNRS-U. Bourgogne, UFR Sciences et Techniques, BP 47870, F-21078 Dijon cedex; <sup>b</sup>Department of Process and Environmental Engineering, P.O.Box 4300, FIN-90014 University of Oulu.

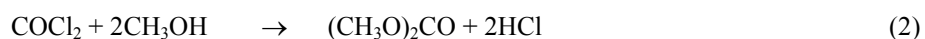
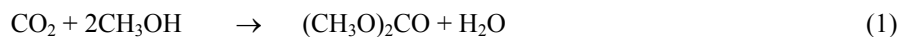
ballivet@u-bourgogne.fr, Fax: + 33 3 80 39 37 72

The pressure effect on the reaction of methanol and carbon dioxide to afford dimethyl carbonate in the presence of *n*-Bu<sub>2</sub>Sn(OCH<sub>3</sub>)<sub>2</sub> was studied in the temperature range 373-423 K. Correlations between reaction kinetics and calculated *P-T* phase diagrams of the binary CO<sub>2</sub>-methanol mixture of different compositions show that supercritical monophasic conditions lead to the highest yield and rate.

## INTRODUCTION

The literature devoted to supercritical carbon dioxide (scCO<sub>2</sub>) for extraction and materials applications is vast in comparison with that for chemical reactions [1]. This field, however, is fast-growing due to opportunities for addressing the modern chemistry issues. Catalyzed reactions are actively studied under these conditions. Both organometallics and heterogeneous catalysts may exhibit rate and selectivity enhancements due to switching rate-limiting step(s), e.g. mass and heat transfer, under monophasic conditions [2-5]. The opposite strategy takes advantage of multiphasic conditions under which the catalyst is insoluble in the scCO<sub>2</sub>-rich phase while the reaction products are soluble. Therefore, it is expected that coupling reaction and separation steps in a single reactor will facilitate catalyst separation and recycling operations. Moreover, such a catalyst immobilization is suitable for continuous-flow operation under multiphasic conditions [6-9].

A particular use of scCO<sub>2</sub> is as solvent and reagent [10]. Coupling its physical and chemical properties allows to take advantage of a reactive solvent. Relevant catalytic examples can be found for the synthesis of cyclic carbonates [11,12] and dimethyl carbonate (DMC) [13-17]. Moreover, the direct synthesis of DMC from carbon dioxide and methanol (eq. 1) avoids the use of hazardous and toxic reagents such as phosgene or carbon monoxide (eqs. 2-3) [18].



Among the catalytic precursors reported so far, organometallic tin(IV) complexes exhibit higher selectivity. The results herein reported concern reaction (1) kinetics in the presence of *n*-Bu<sub>2</sub>Sn(OCH<sub>3</sub>)<sub>2</sub> and correlations with binary CO<sub>2</sub>-methanol fluid phase equilibria for molar compositions used in the catalytic experiments.

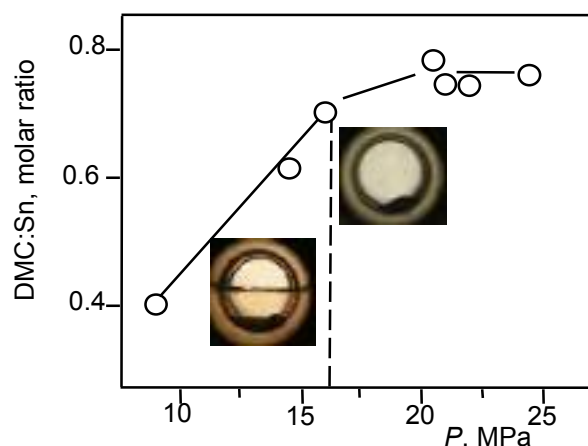
## I-MATERIALS AND METHODS

All reaction and synthetic mixtures were prepared in Schlenk glassware under dry oxygen-free argon. Typical procedure for the kinetics experiments was as follows: the reaction was carried out in a 56-mL stainless steel reactor equipped with a magnetic stirrer, an internal thermocouple, electric heating, and a high-pressure sampling loop (0.090 mL). A 9-mL solution of the tin complex (1.5 mmol) in methanol was introduced by syringe, then liquid CO<sub>2</sub> (Air Liquide N45) with an ISCO 260D pump. At the end of an experiment, the reactor was cooled down to 273 K, pressure gently released, and the liquid phase was transferred for quantitative DMC analysis. Before quenching the reaction at 273 K, a last sampling via the high-pressure loop allowed to check consistency between the two analytical procedures; the fit was better than 3 % (relative error). Quantitative DMC analysis was performed by gas chromatography (Fisons 8000, J&W Scientific DB-WAX 30m capillary column, FID detector, benzene as internal standard). For phase behavior observation, a fixed-volume reactor (46 mL) equipped with sapphire windows (Top Industries S.A., France), a magnetic stirrer, and temperature and pressure gauges was charged with methanol, optionally with the tin complex, DMC and H<sub>2</sub>O, then pressurized with CO<sub>2</sub> to the desired amount with an ISCO 260D pump at room temperature. The temperature was gradually increased up to the visual disappearance of the liquid meniscus, then adjusted and stabilized for 3 h to observed the transition between a non-transparent and a transparent monophasic medium (temperature and pressure readings:  $\pm 1$  K and  $\pm 0.1$  MPa, respectively).

**Caution:** since high pressures are involved, appropriate safety precautions must be taken.

## II-RESULTS AND DISCUSSION

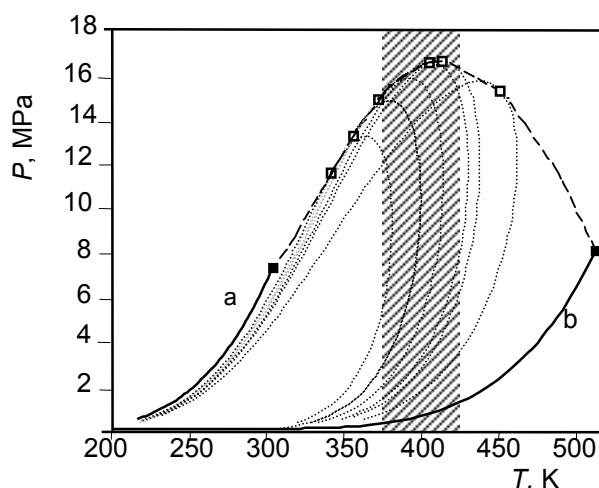
Reaction (1) was conducted with fixed amounts of methanol (230 mmol) and *n*-Bu<sub>2</sub>Sn(OCH<sub>3</sub>)<sub>2</sub> (1.5 mmol) for a reaction time of 20 h at 423 K. The pressure effect on DMC yield was studied by loading CO<sub>2</sub> in the range 46-70 mol%, that allowed to get reaction pressures in the range 8-25 MPa. The results reported in Figure 1 show that DMC formation increases with pressure from 8 to 20 MPa. At higher pressure, 25 MPa, the yield remains practically constant.



**Figure 1:** Pressure effect on DMC formation at 423 K and reaction time of 20 h, and visual observation of phase equilibrium.

The visual observation of the reaction mixture in a reactor equipped with sapphire windows (Figure 1), under the same experimental conditions, shows that the medium is biphasic at  $P < 16.5$  MPa and monophasic at higher pressures.

In order to get a set of liquid-vapor coexistence curves for  $\text{CO}_2$  molar fractions of practical use for our catalytic experiments, we carried out thermodynamic calculations creating  $P$ - $T$  phase diagrams on binary mixtures of methanol-carbon dioxide. Calculations were done with the Flowbat simulation program [19] using the Soave-Redlich-Kwong equation of state [20,21]. The phase envelopes thus obtained for six binary compositions in the range 49.2-89.4  $\text{CO}_2$  mol% are reported in Figure 2. The inside of the envelopes corresponds to the two-phase area where vapor and liquid are in equilibrium. Figure 2 also reports the corresponding critical points (open squares) for each of the six  $\text{CO}_2$ -methanol mixtures. The line drawn through these critical points (dashed line) shows that the critical pressures pass through a maximum at 67.35  $\text{CO}_2$  mol% ( $P_c = 16.61$  MPa,  $T_c = 412.94$  K), while the critical temperature increases monotonically with the methanol content. Moreover, the maximum critical pressure values are much higher than those of the pure components. The dashed area shown in Figure 2 refers to the reaction temperature range.



**Figure 2:** Calculated  $P$ - $T$  diagrams for liquid-vapor coexistence curves and critical points for binary  $\text{CO}_2$ - $\text{CH}_3\text{OH}$  mixtures: (—) liquid-vapour line for (a)  $\text{CO}_2$ , (b)  $\text{CH}_3\text{OH}$ ; (···) two-phase liquid-vapor envelope for binary mixture compositions, from left to right: 89.4, 78.6, 71.3, 67.35, 51.78, 49.2  $\text{CO}_2$  mol%, respectively; (■) CP for (a)  $\text{CO}_2$ , (b)  $\text{CH}_3\text{OH}$ ; (□) CPs of the binary mixtures; (---) binary mixtures critical line). Dashed area: reaction temperature zone.

Comparing Figures 1 and 2, the increase of DMC yield is observed when the reaction mixture exists in a two-phase vapor-liquid equilibrium (8-16.5 MPa). While pressure is passed over the mixtures critical point, increase of pressure do not effect anymore the reaction yield (20-25 MPa).

A kinetic study was performed under biphasic (10 MPa) and monophasic conditions (20 and 25 MPa), at 387 K with initial carbon dioxide loadings of 46 to 70 mol%. From the DMC yield vs time, the initial rate of DMC formation,  $r_0$ , was determined. The values thus obtained,

$0.95 \cdot 10^{-3}$  and  $3.9 \cdot 10^{-3}$  mol h<sup>-1</sup> per Sn (mol L<sup>-1</sup>) under 10 and 20 MPa, respectively, point out a 4-fold increase with pressure. Interestingly, the  $r_0$  value under 25 MPa was identical to that under 20 MPa. These results clearly show that the rate enhancement under monophasic conditions can be ascribed to a positive order in CO<sub>2</sub>.

## CONCLUSION

According to this case study, the reaction benefits from operating conditions under 20 MPa, in the temperature range 373-423 K. As these temperatures are beyond that of the critical point of carbon dioxide ( $T_c = 304.2$  K) and below that of methanol ( $T_c = 512.6$  K), it was relevant to determine whether the reaction takes place under monophasic or multiphasic conditions, for correlating with the kinetics. The thermodynamic  $P$ - $T$  phase diagram calculations of binary CO<sub>2</sub>-CH<sub>3</sub>OH mixtures for our experimental conditions coupled with visual observations revealed that the best yield and rate were obtained under monophasic supercritical conditions. Thus operation in the supercritical domain increased reaction efficiency of this studied organic carbonate synthesis.

## ACKNOWLEDGEMENTS

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