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SYNTHESIS OF DIMETHYL CARBONATE IN SUPERCRITICAL CARBON DIOXIDE

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Abstract - The reactivity of carbon dioxide with methanol to form dimethyl carbonate was studied in the presence of the *n*-butylmethoxytin compounds *n*-Bu_3SnOCH_3, *n*-$Bu_2Sn(OCH_3)_2$, and [*n*-$Bu_2(CH_3O)Sn]_2O$. The reaction occurred under solventless conditions at 423 K and was produced by an increase in CO_2 pressure. This beneficial effect is primarily attributed to phase behavior. The mass transfer under liquid-vapor biphasic conditions was not limiting when the system reached the supercritical state for a CO_2 pressure higher than 16 MPa. Under these conditions, CO_2 acted as a reactant and a solvent.

Keywords: Dimethyl carbonate; Supercritical carbon dioxide; Tin(IV) compounds.

INTRODUCTION

Switching to greener technologies can not only benefit the environment but also increase manufacturing efficiency and reduce waste. Green chemistry includes a number of concepts and principles (Anastas and Warner, 1998), such as waste minimization, solvent selection, atom utilization, catalysis, and alternative synthetic routes from sustainable resources. Therefore, the challenge in fundamental research is to provide tools and understanding for developing new reaction pathways and products according to these principles. For example, linear organic carbonates are interesting target since their conventional production involves the use of toxic phosgene (Shaikh and Sivaram, 1996). One of these, dimethyl carbonate (DMC), has numerous potential applications, avoiding carcinogenic risks of dimethyl sulfate and methyl halides (Tundo, 2001) and the toxicity of phosgene (Rivetti, 2000). Interestingly enough, DMC is considered an option as an oxygenate in reformulated gasoline, but its current price is too high for application (Pacheco and Marshall, 1997).

DMC preparation routes of increasing interest involve carbonate interchange, oxidative carbonylation of alcohols, and carbonation of alcohols (Ballivet-Tkatchenko and Sorokina, 2003). These reactions take place in the presence of catalysts for enhancement of productivity and selectivity. The carbonation reaction is of special interest because the co-reactants are carbon dioxide and methanol. Carbon dioxide is nontoxic, an advantage over phosgene and carbon monoxide, and easy to handle and to store, but much less reactive (Aresta and Quaranta, 1997). However, the implementation of safer technologies justifies the assessment of chemical reactions based on carbon dioxide as it can be viewed as a renewable raw material. Moreover, the use of supercritical carbon

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*To whom correspondence should be addressed dioxide as a substitute solvent has received much attention because of its tunable properties by variation in pressure and temperature (Jessop and Leitner, 1999). Supercritical carbon dioxide may be a particularly advantageous reaction medium when it serves as both a reactant and a solvent (Ballivet-Tkatchenko et al., 2004). The improved rates for catalytic hydrogenation of carbon dioxide support this approach (Jessop et al., 1994). On the other hand, emerging strategies take advantage of multiphasic conditions under which the catalyst is insoluble in $scCO_2$-rich phase and the reaction products, soluble (Ballivet-Tkatchenko et al., 2003). Therefore, cost-effective operations are needed in associating reaction and separation steps in a single reactor. Moreover, recycling of the catalyst is in principle easier.

It has been reported that organometallic compounds based on Sn(IV) can produce reaction (1) with a beneficial effect of CO_2 pressure (Isaacs et al., 1999; Sakakura et al., 1999; Ballivet-Tkatchenko et al., 2000 and 2003).

$$2\,CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (1)$$

However, the reaction mechanism is poorly understood, justifying further studies for improvement of catalyst design.

This paper describes the reactivity of CO_2 with *n*-butylmethoxytin(IV) derivatives and focuses on DMC formation in the presence of methanol under supercritical conditions in accordance with equation (1). Multinuclear magnetic resonance (NMR) and infrared (IR) spectroscopies, and volumetric experiments were used for characterization of the organometallics. The chemical reaction (1) was conducted in the absence of solvent. The effect of additives such as Lewis bases (imidazoles) on the DMC rate as well as the effect of the CO_2 pressure are discussed.

MATERIALS AND METHODS

All experiments were performed under dry oxygen-free argon using Schlenk tube techniques. The solvents were dried over appropriate dessicants and distilled under argon immediately prior to use. The butylstannanes *n*-Bu_3SnOCH_3 and *n*-$Bu_2Sn(OCH_3)_2$ were synthesized from *n*-Bu_3SnCl and *n*-Bu_2SnCl_2 (Aldrich), respectively (Ballivet-Tkatchenko et al., 2000). The butyldistannoxane [*n*-$Bu_2(CH_3O)Sn]_2O$ was obtained by reaction between an equimolar mixture of *n*-Bu_2SnO (Aldrich) and *n*-$Bu_2Sn(OCH_3)_2$ in accordance with the literature (Ballivet-Tkatchenko et al., 2003). Methanol (Aldrich, 99.8+ %) was dried over magnesium methylate. CO_2 N45 TP was purchased from Air Liquide. NMR spectra were recorded at 295 K in deuterated chloroform (Aldrich 99.9 %) on a Bruker Avance 300 spectrometer (^1H = 300.131, ^{119} Sn = 111.910, and ^{13}C = 75.475 MHz). Infrared (IR) spectra were recorded on a Bruker Vector 22 equipped with a Specac Golden Gate^{TM} ATR device.

In a typical experiment under CO_2 pressure, 20 cm^3 of methanol were added to the tin compound (4 mmol based on tin) in a Schlenk tube. Then the solution was transferred to a 120 cm^3 stainless steel batch autoclave. Finally, CO_2 was introduced at 4 MPa, and room temperature. The autoclave was heated up to 423 K (controlled by an internal thermocouple) and the pressure was adjusted to the desired value by a high-pressure CO_2 pump (Top Industrie S.A.). After 12 h of reaction under magnetic stirring, the autoclave was cooled down to 273 Kand depressurized and the condensed phase transferred to a Schlenk tube. A trap-to-trap distillation under vacuum at room temperature allowed separation of the organics, which were analyzed by GC (Fisons 8000, J&W Scientific, DB-WAX 30m capillary column, FID detector), and the tin residue was characterized by multinuclear NMR and IR spectroscopies.

RESULTS AND DISCUSSION

The insertion of CO_2 into Sn-OR bonds of the compounds *n*-Bu_3SnOR, *n*-$Bu_2Sn(OR)_2$, and [*n*-$Bu_2(RO)Sn]_2O$ occurs readily at room temperature (R = CH_3, *i*-C_3H_7). The new species, characterized by multinuclear NMR, IR, volumetry, and elemental analysis, correspond to alkylcarbonate tin(IV) derivatives. The ^{13}C NMR signature of the alkylcarbonato fragment (Sn-OCO_2R) is evidenced by a signal in the 159-156 ppm range. Moreover, a strong IR band due to the CO_3 group is also present at 1660-1600 cm^{-1}. The quantitative determination of carbon dioxide uptake corresponds to the transformation of only one alkoxy group, whatever the number of alkoxy groups originally found around tin. In the di*n*-butyl series, this result is consistent with the ^{119}Sn NMR spectra, which show resonances between –130 and –220 ppm corresponding to pentacoordinated tin atoms (Smith and Tupciauskas, 1978). Accordingly, dimeric structures are proposed as shown in Figure 1.

Recent determinations of $(CH_3)_2Sn(OCH_3)_2$ structure and its carbonated form by single-crystal X-ray diffraction analysis corroborate these assignments (Choi et al., 1999). Therefore, dimers can be viewed as stable structures, either in the solid state or in solution, at room temperature. A modeling study by DFT calculations also shows that the dimer is more stable than the monomer (Ballivet-Tkatchenko et al., 2002). Alkoxy groups ensure this stability due to their oxygen atoms acting as a Lewis base. Only one of the two alkoxy groups is involved in this bonding mode, leaving the other alkoxy moiety in the terminal position. As shown by the X-ray diffraction study, the insertion of CO_2 into the Sn-OCH_3 bond only takes place with the terminal alkoxy due to the higher basicity of the oxygen atom. The stannyl carbonate fragment Sn-OCO_2CH_3 thus formed is reversibly converted to the starting Sn-OR species under vacuum at room temperature. This property is of primary importance for the reactivity of the system for DMC formation.

The adducts with n-Bu_3SnOR and $[n$-$Bu_2(RO)Sn]_2O$ are more stable; the quantitative de-insertion of CO_2 is now observed under vacuum treatment between 303 and 363 K, depending on the R group. The $[n$-$Bu_2(RO)Sn]_2O$ compound also has a dimeric structure as well as its carbonated form (Figure 2).

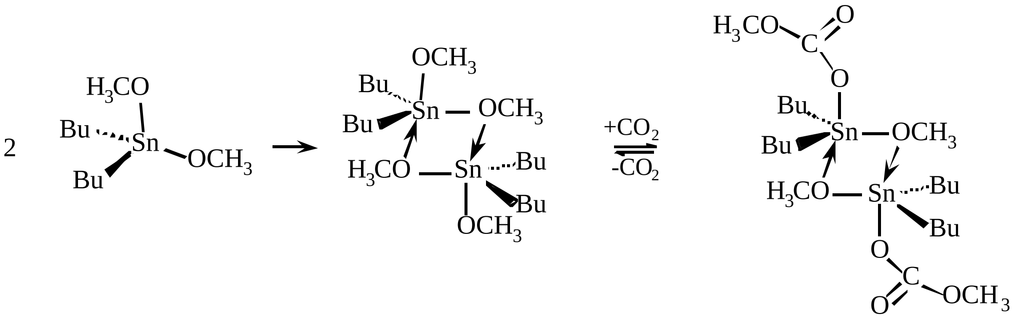

Figure 1: Dimeric structures of n-$Bu_2Sn(OCH_3)_2$ and n-$Bu_2Sn(OCO_2CH_3)(OCH_3)$.

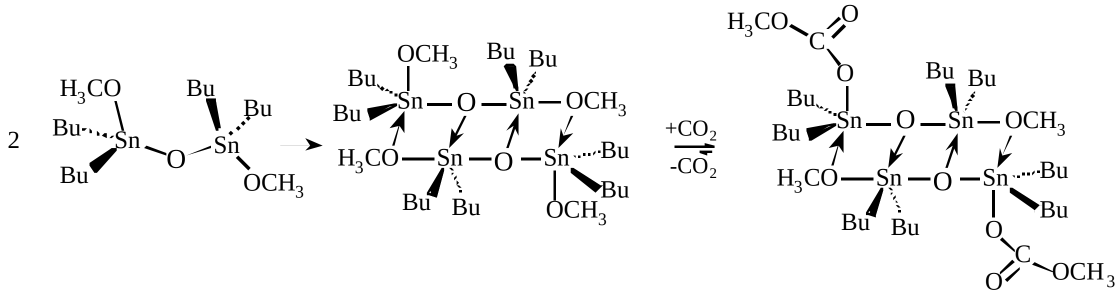

Figure 2: Dimeric structures of $[n$-$Bu_2(CH_3O)Sn]_2O$ and n-$Bu_2(CH_3O)SnOSn(OCO_2CH_3)$ n-Bu_2.

In this distannoxane series, alkoxy and oxo groups ensure the stability of the dimeric form through four coordination bonds. Such structures are well documented for tetraorganodistannoxanes and related systems (Chandrasekhar et al., 2002).

When the compounds n-$Bu_2Sn(OCH_3)_2$, $[n$-$Bu_2(CH_3O)Sn]_2O$, and n-Bu_3SnOR were dissolved in methanol and then mixed with CO_2, and heated in a batch reactor for 12 h, DMC is selectively formed with a maximum yield at 423 K. The order of reactivity found, n-$Bu_2Sn(OCH_3)_2$ > $[n$-$Bu_2(CH_3O)Sn]_2O$ > n-Bu_3SnOR, indicates that the best DMC yield is obtained for the compound having two methoxy groups per tin (Table 1, entries 1-3). Concomitantly, the DMC:Sn molar ratio is close to one.

Table 1: DMC yield with *n*-butylmethoxytin(IV) compounds in methanol at 20 MPa and 423 K (Sn = 4 mmol, CH_3OH = 20 cm^3, *t* = 12 h).

Entry	Tin Compound	Additive (molar ratio)	DMC:Sn molar ratio
1	$n\text{-}Bu_3SnOCH_3$		0.12
2	$[n\text{-}Bu_2(CH_3O)Sn]_2O$		0.56
3	$n\text{-}Bu_2Sn(OCH_3)_2$		0.90
4	$n\text{-}Bu_2Sn(OCH_3)_2$	HIm (1:1)	0.70
5	$n\text{-}Bu_2Sn(OCH_3)_2$	HIm (2:1)	0.82
6	$n\text{-}Bu_2Sn(OCH_3)_2$	1-MeIm (2:1)	0.93
7	$n\text{-}Bu_2Sn(OCH_3)_2$	1-MeIm (4:1)	0.81

This result is in agreement with the carbonation of only one methoxy group (Figures 1, 2). CO_2 pressure effect was also found to have an effect. Increasing the pressure from 9 to 20 MPa led to a progressive increase in DMC yield from 0.4 to 0.9 (DMC:Sn molar ratio). A further increase up to 25 MPa had no effect. Several explanations can account for this observation. On the one hand, as the CO_2 adduct is reversible, the carbonated species should be favored at higher pressures and on the other hand, the phase diagram of the reaction mixture may be such that phase changes may occur in this pressure range.

As we had no opportunity to perform spectroscopic measurements at 423 K and 20 MPa, we decided to check the first hypothesis by changing the electronic properties of tin in adding Lewis bases such as imidazole (HIm) and 1-methylimidazole (1-MeIm) to the reaction mixture. Coordination of imidazoles is known for Sn(IV) compounds forming 1:1 and 2:1 adducts (Pettinari, 1999). If coordination occurs under the reaction conditions, the monomeric form $n\text{-}Bu_2Sn(OCH_3)_2$ will be stabilized and the two methoxy groups, carbonated. Therefore, the DMC:Sn ratio will reach a value of two. The results reported in Table 1 (entries 4-7) show no drastic alteration in the DMC yield with imidazoles as additives.

The study of the phase diagram was more informative. In this work, the pressures applied ranged from 9 to 25 MPa. They are beyond the critical pressures of CO_2 and methanol, 7.38 and 8.09 MPa, respectively, but the reaction temperature (423 K) is in between the critical temperatures of CO_2 (Tc = 304.2 K) and methanol (Tc = 512.6 K). Accordingly, the binary mixture may undergo phase changes in pressure and CO_2-methanol composition. The liquid-vapor (LV) case consists in a methanol-rich liquid phase in which the tin compounds are soluble. The chemical reaction will therefore take place in the liquid phase. The solubility of CO_2 in methanol has been reported to decrease with increasing temperature and to increase with pressure (Chang et al., 1997). Accordingly, in our study under isothermal conditions an increase in CO_2 pressure will shift the equilibria depicted in Figures 1 and 2 to the carbonated specie thus enhancing the rate of DMC formation, in agreement with the experimental results. However, the biphasic LV regime may no longer be valid for high pressures. One might expect to switch to monophasic conditions. Hence, this phase effect may be superimposed.

The CO_2-methanol phase behavior has been investigated by a number of researchers. Data available for the conditions defined in our study (423 K, 60 < CO_2 < 76 mol%) point to a corresponding critical pressure of around 16 MPa (Wells et al., 2003). In order to discover to what extent the addition of tin compounds affects the system, the phase behavior of the three-component mixture was visually examined by conducting the reaction in a 30 cm^3 stainless steel autoclave equipped with sapphire windows (Top Industrie S. A.). We observed the changes at the liquid-vapor interface while heating the reactor from room temperature to 423 K with an initial CO_2 composition of 76% (mol), providing a final pressure of 23 MPa at 423 K. The autoclave was loaded with a methanolic solution of 0.47% (mol) $n\text{-}Bu_2Sn(OCH_3)_2$ at room temperature and then CO_2 was added. Upon addition, the liquid phase expanded due to CO_2 absorption. Heating led to the progressive shrinking of the liquid phase. The merging of the liquid and vapor phases was observed around 16 MPa and 410 K. Hence, on the basis of this observation, the increase in DMC rate with CO_2 pressure occurs with a phase change from a biphasic LV system to a monophasic supercritical one. The benefit arises from the reactants being in a single-fluid phase so that the chemical reaction occurs homogeneously, avoiding CO_2 mass transfer limitations. At the present level of our understanding, it is the most important contribution of the supercritical conditions. However, specific solvation properties of the supercritical fluid should not be underestimated (Brennecke and Chateauneuf, 1999) and further work in this direction is in progress.

CONCLUSIONS

The carbonation of methanol to form dimethyl carbonate in the presence of *n*-butylmethoxytin compounds was achieved under solventless conditions at 423 K. Mass transfer of gaseous CO_2 into the methanolic solution was limited under liquid-vapor biphasic conditions. The rate of DMC formation was lower than under monophasic conditions. The single-fluid phase was reached by increasing CO_2 pressure, resulting in a supercritical medium where CO_2 acted as a reactant and a solvent. This case study herein described highlights of optimization of a chemical reaction that can be achieved by controlling the phase behavior of the mixture. The benefit of increasing the rate and selectivity is regularly emphasized by experts in the domain of supercritical fluids. The main information still needed is the description of phase equilibria existing in the reactor as a function of pressure and temperature. This objective requires an interdisciplinary approach with complementary expertise in synthetic chemistry, analytical chemistry, and chemical engineering.

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NOMENCLATURE

n-Bu	normal butyl chain
^{13}C NMR	carbon-13 nuclear magnetic resonance spectroscopy
CH_3	methyl
i-C_3H_7	isopropyl
CO_2	carbon dioxide
DFT	density functional theory
DMC	dimethyl carbonate
HIm	imidazole
IR	infrared spectroscopy
LV	liquid-vapor
1-MeIm	1-methylimidazole
mol	mole
NMR	nuclear magnetic resonance spectroscopy
CH_3O	methoxy group
P	pressure (MPa)
Pc	critical pressure (MPa)
ppm	NMR chemical shift in part per million
R	alkyl group
sc	supercritical
^{119}Sn NMR	tin-119 nuclear magnetic resonance spectroscopy
T	temperature (K)
Tc	critical temperature (K)
t	time (h)

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