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Selective Conversion of Carbon Dioxide to Dimethyl Carbonate by Molecular Catalysis

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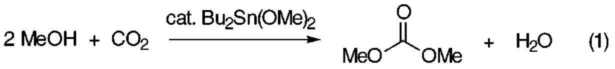
The development of an environmentally friendly industrial process utilizing carbon dioxide, which is the most abundant carbon resource and a greenhouse compound, as a cheap and safe C_1 building block as well as a nontoxic reaction media has drawn much interest.[1,2] Especially, the possibility as a phosgene alternative is quite attractive.[3] Our synthetic target starting from carbon dioxide is dimethyl carbonate (DMC). Applications of DMC range from polycarbonate synthesis via diphenyl carbonate to methylating reagents, carbonylating reagents, solvents, octane boosters in gasoline, carbon-particle reducing agents for diesel engines, and so on.[4] The historical synthetic route to DMC is based on the methanolysis of toxic and corrosive phosgene. Recently, another route to DMC was developed using CO under oxidative conditions.[4,5] However, CO is also highly toxic and flammable. Hence, CO_2 is obviously the ideal carbonyl source for carbonates.

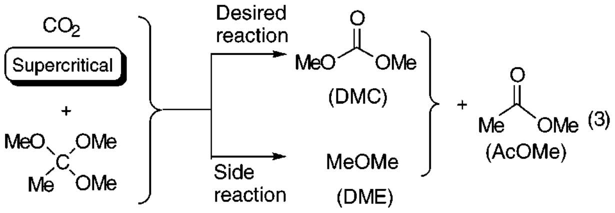
A considerable amount of effort has already been devoted to producing DMC from methanol and CO_2, and some of the reactions were catalyzed by organotin alkoxides (eq 1).[6] However, the catalytic activities so far obtained have been very low (less than a few turnovers) due to the decomposition of the catalysts by water (coproduct) (eq 2). In the last several years, researchers in the Czech Republic intensively reinvestigated this reaction with regard to various promoters and also many kinds of drying agents, resulting in no remarkable progress.[6a−c] Although several other approaches for carbonate synthesis from CO_2 were also proposed, the performance of those processes is still unsatisfactory.[7]



$$Bu_2Sn(OMe)_2 + H_2O \longrightarrow Bu_2SnO + 2\ MeOH \qquad (2)$$

Hence, we need some new methodologies to improve the efficiency of catalytic CO_2 conversion. Our idea is rather simple. Instead of removing water after the reaction (eq 1), we first dehydrate MeOH and then react the resulting dehydrated derivatives with CO_2 to produce DMC. Typical dehydrated derivatives of methanol are dimethyl ether, dimethyl acetal (ketal), and trimethyl ortho ester. Since reactivity should be increased in this order, we first tried the reaction of the most reactive compound, the ortho ester.

We report here the selective DMC synthesis via the reaction of supercritical CO_2 and trimethyl orthoacetate. The reaction pattern can be summarized in eq 3. The desired reaction gives DMC and methyl acetate, while the side reaction results in the formation of dimethyl ether and methyl acetate. Although complex-catalyzed reactions of CO_2 with high-energy chemicals such as oxiranes, oxetanes, diynes, and dienes are well documented,[1,3] reactions with saturated compounds have not been well developed except for hydrogenation.[8]



On the basis of the previous results of the DMC synthesis from methanol and CO_2,[6,7] we examined the combination of metal alkoxides and some promoters as catalytic systems. The results are summarized in Table 1 (Ts, *p*-toluenesulfonyl; Cp, cyclopentadienyl, Cp*, pentamethylcyclopentadienyl).[9] In all the cases, material balance was satisfactory: the sum of remaining ortho ester and produced methyl acetate was nearly 100% based on the starting ortho ester. Hence, the DMC/AcOMe ratio reasonably represents the selectivity of the reaction.

The reaction strongly depends on the structure of metal alkoxides. For example, although dibutyltin dimethoxide catalyzes the reaction selectively (entry 1), use of tributyltin methoxide resulted in virtually no reaction (entry 2). Dimethyltin dimethoxide was less effective compared with the dibutyltin derivative. On the other hand, addition of tetrabutylammonium *p*-toluenesulfonate

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[2] As for the general properties of supercritical CO_2 as a solvent for metal-catalyzed reactions, see: (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065−1069. (b) Tumas, W.; et al. In *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society, Washington, DC, 1996; pp 132−151.

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[8] (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259−272. (b) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207−2221.

[9] (a) A part of this work was presented at the 9th IUPAC Symposium for Organometallic Chemistry Directed towards Organic Synthesis (OMCOS-9), Göttingen, Germany, July 20−25, 1997; International Union of Pure and Applied Chemistry; Abstract SL-25. (b) We have also found that onium salts alone promote eq 3; see: 44th Symposium on Organometallic Chemistry, Osaka, Japan, September 20−21, 1997; Kinki Chemical Society; Abstract B209. (c) A relevant patent has appeared recently: Ko, K.; Ogata, F. (Showa Denko) JP-A2 07224010 [*Chem. Abstr.* **1996**, *124*, 86370].

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Table 1. DMC Synthesis from CO_2 and Trimethyl Orthoacetate[a]

entry no.	metal complex	additive	temp (°C)	yield[b] (%)	sel (%) DMC/AcOMe
1	$Bu_2Sn(OMe)_2$	none	180	20	93
2	$Bu_3Sn(OMe)$	none	180	>1	36
3	$Me_2Sn(OMe)_2$	none	180	7	96
4	$Bu_2Sn(OMe)_2$	Bu_4NOTs	180	48	85
5	$Bu_2Sn(OMe)_2$	Bu_4PI	180	70[c]	75
6	$Cp_2Ti(OMe)_2$[d]	Bu_4PI	150	37	58
7	$Cp^*{}_2Ti(OMe)_2$[d]	Bu_4PI	150	47	75

[a] Reaction conditions. Ortho ester (50 mmol), metal complex (0.85 mmol), additive (0.85 mmol), 300 atm, 24 h at reaction temperature. [b] Based on the ortho ester. [c] After 72 h. [d] Formed in situ from Cp_2MCl_2 or $Cp^*{}_2MCl_2$ and $Mg(OMe)_2$ (0.85 mmol) in MeOH (1.2 cm^3).

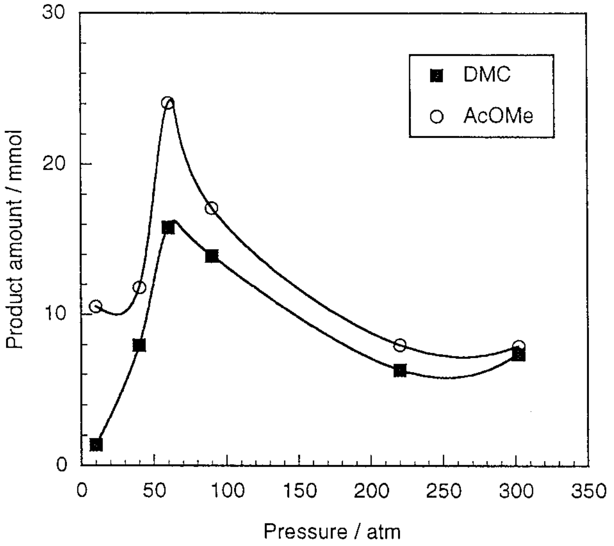

Figure 1. Pressure effect on the $Bu_2Sn(OMe)_2-Bu_4PI$ system (150 °C, 24 h).

substantially enhanced the catalytic activity (entry 4). Other effective onium salts are tetrabutylammonium iodide, tetrabutylphosphonium iodide, and so on. DMC yield reached 70% after a longer reaction time (entry 5). It is also worth noting that Bu_2SnI_2 was essentially inactive under these conditions. The phase behavior of the reaction mixtures was investigated using a reaction vessel equipped with sapphire windows. The reaction mixture catalyzed by $Bu_2Sn(OMe)_2$ alone was completely homogeneous throughout the reaction (entry 1). However, insoluble oily droplets were observed on the wall in the catalytic systems containing onium salts (entries 4 and 5). Catalytic systems composed of titanium complex and onium salt also produced DMC. However, the selectivity obtained by the Cp complex (entry 6) was considerably lower than those realized by the tin-based system. An interesting thing here is by changing the ancillary ligand, Cp to a bulkier Cp* ligand, we could improve both catalytic activity and selectivity (entry 7).

The results shown in Table 1 were obtained using CO_2 under supercritical conditions. Then, what will happen if the reaction is conducted below critical pressure using gaseous CO_2? The pressure effect was studied using the tin–iodide system, and the result is summarized in Figure 1. The empty circle is the amount of AcOMe, and the black square represents DMC yield. We can conclude two things here. First, catalytic activity becomes highest around the critical pressure of CO_2 (73 atm). A similar phenomenon was observed in metal-catalyzed oxidation of cyclohexane in supercritical CO_2.[10] Second, to get a higher selectivity, higher pressure in the supercritical region is preferable. The latter phenomenon is reasonably related to the side reaction to form dimethyl ether (DME), a byproduct without the incorporation of CO_2. Indeed, the larger amount of dimethyl ether was detected when the selectivity was lower.

Although we have not yet made sufficient mechanistic studies, the following compounds were observed in reaction mixtures of the tin–iodide system and characterized by GC–MS: MeI, MeOMe, $MeCO_2Me$, DMC, CO_2, and $MeC(OMe)_3$. On the other hand, insertion of carbon dioxide into the metal–oxygen bond of $Bu_2Sn(OMe)_2$, in other words, nucleophilic attack of the metal–alkoxide to CO_2, produces a carbonate complex.[11] Thermal decomposition of the metal carbonate or reaction with an electrophile such as methyl iodide possibly results in DMC formation.

In summary, this work demonstrates the promising prospect of carbon dioxide as a phosgene substitute in molecular catalysis, especially under supercritical conditions. We are also eager to develop new functionalization treatments of gaseous molecules (methane, ethane, propane, carbon dioxide, etc.) by molecular catalysis under liquefied or supercritical conditions. Such an approach seems hopeful to transform underutilized gaseous carbon resources into industrially useful compounds.[12]

Experimental Section

General Methods. Trimethyl orthoacetate, dibutyltin dimethoxide, tributyltin methoxide, bis(cyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl)titanium dichloride, magnesium dimethoxide (methanol solution), tetrabutylammonium *p*-toluenesulfonate, and tetrabutylammonium iodide were purchased from Aldrich Chemical Co. (Milwaukee, WI). Carbon dioxide (Showa Tansan Co., Kawasaki, purity over 99.9%, water content less than 0.01%) was used without further purification. Tetrabutylphosphonium iodide,[13] dimethyltin dimethoxide,[14] and dibutyltin diiodide[15] were synthesized according to the literature methods. Reaction products were analyzed by GC using capillary columns: J & W Science DB-WAX (30 m), GL Science TC-WAX (60 m), and Hitachi DDP-90 (90 m) on a Shimadzu 14B, 17A, or 4C gas chromatograph equipped with a flame ionization detector (FID) using 1,3,5-trimethylbenzene as an internal standard. All the volatile products were also characterized with GC–MS using a HP-5890 gas chromatograph connected to a HP-5971A mass spectrometer (EI 70 eV).

General Procedure. All manipulations were carried out under purified argon. In a stainless steel autoclave (20 cm^3 inner volume), carbon dioxide (liquid, 65 atm) was added to a mixture of trimethyl orthoacetate (6.3 cm^3, 50 mmol), a metal alkoxide (0.85 mmol), and an onium salt (0.85 mmol) at room temperature. The autoclave was heated in an oil bath; the initial pressure was adjusted to 300 atm at reaction temperature. After cooling, 1,3,5-trimethylbenzene (50 μL) was added to the reaction mixture as an internal standard in order to determine product yields by GC. Products were further identified using GC–MS by the comparison of retention times and fragmentation patterns with authentic samples.

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