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Tin Tetra(*tert*-butoxide) with Acid–Base Additives: Valid Catalyst Precursors for Direct Synthesis of Dimethyl Carbonate from CO_2 and CH_3OH

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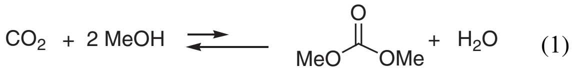
$Sn(Ot\text{-}Bu)_4$ is a user-friendly precatalyst for the direct synthesis of dimethyl carbonate from CO_2 and MeOH. It is far more active than the conventional $Bu_2Sn(OMe)_2$ catalysts. The addition of acid and/or base cocatalysts as well as optimization of the CO_2 pressure improved the catalytic activity. The reaction is proposed to proceed through the formation of a dimeric intermediate composed of six-coordinated tin carbonate complexes.

The conversion of abundant CO_2 into industrially valuable chemicals, such as dimethyl carbonate (DMC), is an imperative research theme from the viewpoint of green-sustainable chemistry.[1] DMC is a much anticipated substance as methylation and acetylation agents for fine chemicals synthesis, a precursor for the synthesis of polycarbonates or polyurethanes, an electrolyte solvent for lithium ion batteries, a fuel additive, etc. Although DMC has been practically synthesized using highly toxic agents, such as phosgene and CO, a more environmentally friendly process using CO_2 and MeOH producing water as the sole by-product has been strongly desired.



$$CO_2 + 2\,MeOH \rightleftharpoons MeO\text{–}C(=O)\text{–}OMe + H_2O \qquad (1)$$

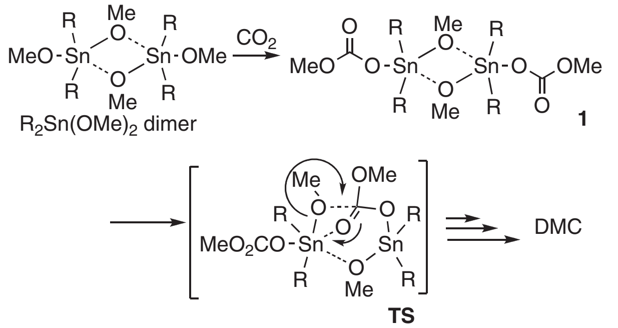
$$(\Delta H = -5.6\,\mathrm{kcal\,mol^{-1}}, \Delta G\ (\text{at } 100\,°\mathrm{C}) = 12.2\,\mathrm{kcal\,mol^{-1}})^2$$

After the discovery of $Bu_2Sn(OR)_2$[3] as a catalyst for the reaction, various metal oxides, such as ZrO_2,[4a–4c,5] CeO_2,[4d–4g] and SnO_2,[5] as well as metal alkoxides, such as $Sn(OR)_4$,[6,7a] $Ti(OR)_4$,[7a,8a,8b] $Nb(OR)_5$,[9] supported metal catalysts,[10] and others[11] have been developed.

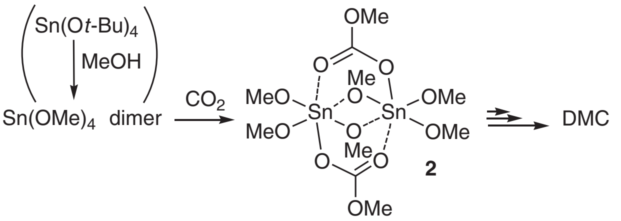
However, the DMC formation of eq 1 is thermodynamically disadvantageous due to the positive ΔG value so that not only the turnover number (TON) of the catalysis but also the DMC chemical yield are limited whatever catalyst is used. In order to overcome the equilibrium limitation, diverse trials employing various inorganic or organic dehydrating agents,[7b,7c] such as Na_2SO_4, molecular sieves, dicyclohexylcarbodiimide, acetals, and nitriles, have been proposed. Especially, reproducible $Me_2C(OMe)_2$ for $Bu_2Sn(OMe)_2$[8c] and nitriles for CeO_2[4e–4g] were found to be more efficacious dehydrating agents for producing DMC in excellent yields.

The reaction rate of the DMC formation still needs to be improved, in other words, the activation energy of the rate-limiting step, which is strongly dependent on the catalyst, must be lowered. Therefore, a more in-depth contemplation of the reaction intermediates and transition states in the catalytic cycle leading to the DMC formation is essential.

Among the metal alkoxide catalysts, $R^1{}_2Sn(OR^2)_2$ is the most promising and well-investigated.[3,4,7a,7b] For instance, how the DMC yield is influenced by the presence of dehydrating agents[8c–8e] and additives,[8a] as well as CO_2 pressures[8f] has been reported. The study of the $R^1{}_2Sn(OR^2)_2$-catalyzed DMC synthesis proposed that the reaction proceeded through dimeric tin complexes[12] because $M(OR)_nY_{4-n}$ ($n = 1$–4) are apt to dimerize (or oligomerize) when the radii of M and R are small.[13] This catalytic mechanism was further validated by the identification of the $R_4Sn_2(\mu^2\text{-}OMe)_2(OCOOMe)_2$ (**1**) intermediate including two five-coordinated tin atoms by ^1H, ^{13}C, ^{119}Sn NMR, and single-crystal X-ray diffraction.[8g] The relevant DFT calculation study claimed that a concerted reaction of an attack of a carbonyl oxygen in the carbonate ligand on the tin atom and the simultaneous attack of a methoxy ligand on the carbonyl carbon (Scheme 1, TS) required the highest activation energy for the DMC synthesis.[14]



Scheme 1. Generally accepted reaction scheme for direct DMC synthesis using conventional $R_2Sn(OMe)_2$ catalyst.



Scheme 2. Plausible reaction scheme for direct DMC synthesis using $Sn(Ot\text{-}Bu)_4$ catalyst.

So far, the activity of $R^1{}_2Sn(OR^2)_2$ is insufficient for industrial application, and the toxicity of organotins is another concern. $Sn(OR)_4$ (R = Me, Et, and *n*-Bu) catalysts were reported to show DMC yields comparable to $R^1{}_2Sn(OR^2)_2$.[6,7a] Although $Sn(OR)_4$ is less toxic, $Sn(OR)_4$ is more easily hydrolyzed than $R^1{}_2Sn(OR^2)_2$. Therefore, investigations of the catalysis of $Sn(OR)_4$ for DMC synthesis had been suspended after Kizlink et al. concluded that the dialkyltin complexes were more convenient for use than the less stable tetraalkoxides.[7a]

However, we envisaged that the catalysis of $Sn(OMe)_4$ would be much better than that of $R_2Sn(OMe)_2$, comparing the plausible reaction pathways using $Sn(OMe)_4$ and $R_2Sn(OMe)_2$.[15] In the $Sn(OMe)_4$ system, the intermediate species corresponding to **1** in the $R_2Sn(OMe)_2$ system would be **2**, in which each methoxycarbonate (–OCOOMe) group on one tin atom can coordinate to the other tin to stabilize the six-coordinated tin complex with a local minimum energy (Scheme 2).[15] Therefore, the CO_2 insertion into an Sn–OMe bond of a dimer of $Sn(OMe)_4$ would be promoted by the formation of the stabilized **2**. It is also expected that the rate-limiting step with a lower activation energy than that of $R_2Sn(OMe)_2$ will follow the formation of **2**. It should be noted that **2** has more exchangeable spectator ligands, which only exert electronic and steric influences on the tin atoms, than **1**, which has only one exchangeable spectator ligand other than inert alkyl groups. Therefore, intermediate **2** can be tuned with some additives that lead to a better catalysis for the DMC synthesis than intermediate **1**.

$Sn(OMe)_4$ was first synthesized and used for the DMC synthesis without additives or dehydrating agents. However, no reproducible results were obtained probably because $Sn(OMe)_4$ was apt to be hydrolyzed (see Supporting Information).[16] Next, we turned our attention to $Sn(Ot\text{-}Bu)_4$, because $Sn(Ot\text{-}Bu)_4$ is monomeric unlike other tin primary alkoxides and easily purified by distillation. In addition, $Sn(Ot\text{-}Bu)_4$ is in situ convertible into the corresponding tin methoxides in contact with MeOH.

$Sn(Ot\text{-}Bu)_4$ was prepared from $SnCl_4$ and *t*-BuOH in the presence of Et_2NH,[17] purified by distillation (bp: 85 °C/40 Pa), and obtained as a white waxy solid (mp: ca. 40 °C). The catalyst (0.25 mmol), additives (50 mol % of catalyst), and dry MeOH (2 mL, 49 mmol) were added to a 10-mL autoclave. After introducing 4 MPa of CO_2, the autoclave was heated at 150 °C, and the interior pressure was adjusted to a given value. After the reaction mixture in the autoclave was stirred for a given time, the autoclave was cooled to −78 °C, and the CO_2 gas was gently released. The reaction products were transferred in a vacuum in order to separate off the high-boiling components and collected. The DMC yield was determined by GC analysis.

The reaction using $Sn(Ot\text{-}Bu)_4$ proceeded much faster than that using $n\text{-}Bu_2Sn(OMe)_2$ as shown in Figure 1 and Table 1, Runs 1 and 8. Based on a GC-MS analysis of the reaction mixture, it was confirmed that almost all the *t*-BuO groups (>3.5 equiv/Sn) were displaced and detected as *t*-BuOH. No *t*-BuO(CO)OMe or *t*-BuO(CO)O*t*-Bu were observed, while RO(CO)OMe and RO(CO)OR were reported to be produced when $M(OR)_4$ (M = Ti or Sn, R = Et, *n*-Bu) were applied.[6,7a] This implies that the *t*-BuO group was not able to occupy the bridging position between the two tin atoms and that the insertion of CO_2 into an Sn–O*t*-Bu bond would be very slow or would not take place.

The time course of the DMC formation in the absence of dehydrating agents revealed that the reaction had an induction period of ca. 1 h (Figure 1).[18] It is reasonable that tin butoxide takes some time to be converted into the corresponding methoxides. The reaction rate then abruptly increased but slowed down when the yield reached 90% at 24 h. Therefore, the catalytic activities under the following different conditions were estimated by comparing the yields at 3 h as the "pseudo reaction rate".

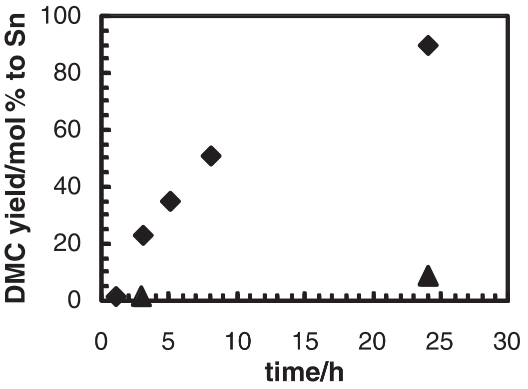


Figure 1. The time course of DMC formation from CO_2 and MeOH using $Sn(Ot\text{-}Bu)_4$ (◆) and $n\text{-}Bu_2Sn(OMe)_2$ (▲).

Table 1. DMC synthesis from CO_2 and MeOH using $Sn(Ot\text{-}Bu)_4$ or $Bu_2Sn(OMe)_2$ with various additives[a]

Run	Catalyst	Additive	DMC yield to Sn/%
1	$Sn(Ot\text{-}Bu)_4$	None	24
2		Pyridine	32
3		PhOH	42
4		PhOH + Pyridine	45
5		Ph_2NH_2OTf	3.4
6		C_6F_5OH	39
7		C_6F_5OH + Pyridine	60
8	$Bu_2Sn(OMe)_2$	None	1.1
9		Ph_2NH_2OTf	20

[a]Reaction time is 3 h.

The effects of acid or base additives were then investigated by comparing the yields at 3 h (Table 1). While Ph_2NH_2OTf was reported to be the most effective for $Bu_2Sn{=}O$,[19] it gave a poor result (Run 5 vs. 9), implying that the reaction mechanism of $Sn(OR)_4$ seems to be different from that of $R_2Sn(OMe)_2$. The addition of PhOH or pyridine increased the reaction rates (Runs 2 and 3). The addition of both PhOH and pyridine gave a slight enhancement (Run 4). Using C_6F_5OH instead of PhOH had almost the same effect (Run 6), but the combined use of C_6F_5OH and pyridine gave the highest yield of 60% (Run 7). Other additives, such as *N*,*N*-dimethylaminopyridine, bipyridine, stearic acid, and catechol, were ineffective (not shown).

The dependence of the catalytic activity of $Sn(Ot\text{-}Bu)_4$ on the CO_2 pressure is shown in Figure 2. Although it was reported that the catalytic activity of $R_2Sn(OMe)_2$ monotonously improved as the CO_2 pressure increased up to 20 MPa,[12] that of $Sn(Ot\text{-}Bu)_4$ showed its maximum at 7.5 MPa. This is possibly because the insertion of CO_2 into the Sn–OMe bond more readily takes place in the $Sn(OMe)_4$ system than that in $R_2Sn(OMe)_2$ due to the formation of the stabilized intermediate **2** by the double coordination of the carbonate groups around the tin atoms.

The addition of a dehydrating agent of 2,2-dimethoxypropane ($Me_2C(OMe)_2$; DMP) was also found effective in the case of $Sn(Ot\text{-}Bu)_4$. The yield at 24 h in the presence of C_6F_5OH and pyridine as well as DMP at 20 MPa was 236%, which was twice as high as that without the dehydrating agent. This indicates the

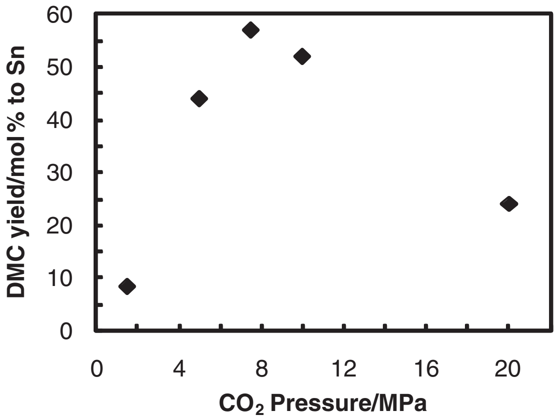


Figure 2. Dependence of the catalytic activity of $Sn(Ot\text{-}Bu)_4$ on the CO_2 pressure in DMC synthesis from CO_2 and MeOH; reaction time is 3 h.

catalysis of $Sn(Ot\text{-}Bu)_4$ is not only much "faster" than that of $R_2Sn(OMe)_2$, but also the addition of the dehydrating agent to $Sn(Ot\text{-}Bu)_4$ effectively advances the DMC formation.

In conclusion, we found a distillable, less-toxic $Sn(Ot\text{-}Bu)_4$ to be an easily handled, reliable precatalyst for the synthesis of DMC from CO_2 and MeOH. The catalytic activity of $Sn(Ot\text{-}Bu)_4$ was far higher than that of a conventional $Bu_2Sn(OMe)_2$ catalyst. With the concurrent addition of acid and base cocatalysts, C_6F_5OH and pyridine, the highest increase in the catalytic activity was observed. $Sn(Ot\text{-}Bu)_4$ showed its optimal CO_2 pressure of 7.5 MPa for the DMC synthesis that is a very different tendency from that reported for $R_2Sn(OMe)_2$, in which the catalytic activity increases with the higher CO_2 pressures. The dependence of the catalytic activity on the CO_2 pressure and the type of efficacious additives are different from those for the $R_2Sn(OMe)_2$ catalyst, suggesting that the reaction mechanism, especially concerning the rate-limiting step, is different from that of $R_2Sn(OMe)_2$.

In the catalytic system of $Sn(Ot\text{-}Bu)_4$, a dimeric intermediate **2** composed of six-coordinated tin complexes is possibly formed, while in $R_2Sn(OMe)_2$, **1** having five-coordinated tins is an intermediate complex. The insertion of CO_2 into the dimeric complex of $Sn_2(OMe)_8$ and the subsequent concerted processes to afford DMC should be more efficiently promoted than those in $R_2Sn(OMe)_2$. It is also considered that the rate-limiting step with a lower activation energy will follow the formation of **2**. More precise quantum chemical studies on the catalytic mechanism for the $Sn(Ot\text{-}Bu)_4$-catalyzed DMC synthesis are under way.[15]

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15 We carried out the calculations using the Hartree–Fock method with a combination of LANL2DZ basis set for tin atoms and 6-31G** for the other atoms. A higher level quantum chemical calculation is now under way: Y. Masui, S. Haga, M. Onaka, to be published elsewhere.

16 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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18 It takes some induction time a) to heat the stainless autoclave to 150 °C by an air heater, b) to convert $Sn(Ot\text{-}Bu)_4$ into $Sn(OMe)_4$, and c) to insert CO_2 into the $Sn(OMe)_4$ dimer.

19 $n\text{-}Bu_2Sn(OMe)_2$ is formed by the reaction of $Bu_2Sn{=}O$ with MeOH. The activity of $Bu_2Sn{=}O$ was reported to be comparable to that of $n\text{-}Bu_2Sn(OMe)_2$ in ref 8f.