ELSEVIER

Note

Reaction of dibutyltin oxide with methanol under CO_2 pressure relevant to catalytic dimethyl carbonate synthesis

Kazufumi Kohno, Jun-Chul Choi, Yoshihiro Ohshima, Abulimiti Yili,
Hiroyuki Yasuda, Toshiyasu Sakakura *

National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Abstract

Dibutyltin oxide $(Bu_2SnO)_n$ (**3**) reacts with methanol to give the tetrabutyl(dimethoxy)stannoxane dimer (**4**). The presence of 2,2-dimethoxypropane under a CO_2 pressure accelerates the reaction resulting in nearly quantitative yield. Complex **4** exhibits catalytic activity as high as that of $\{Bu_2Sn(OMe)_2\}_2$ (**1**) in the dimethyl carbonate (DMC) synthesis from CO_2 and methanol. These results indicate that the conversion of **3** to **4** occurs under catalytic DMC production conditions.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide; 2,2-Dimethoxypropane; Tetrabutyl(dimethoxy)stannoxane dimer

1. Introduction

Dimethyl carbonate (DMC) is a key compound in so-called green chemistry. DMC itself is also useful as an electrolyte for lithium ion batteries and a fuel additive [1]. Moreover, DMC is also very important as an environmentally benign synthetic reagent because it works as a substitute for toxic conventional methylating and carbonylating reagents such as methyl iodide, methyl sulfate, carbon monoxide, etc. [2,3]. It is an especially effective substitute for phosgene; e.g. intermediates for polycarbonates or polyurethanes [4,5].

Several processes have been proposed to industrially synthesize DMC [6]: (1) reaction of phosgene with methanol, (2) reaction of carbon monoxide with methanol in the presence of oxygen (oxidative carbonylation) [7], (3) reaction of ethylene oxide with CO_2 to produce ethylene
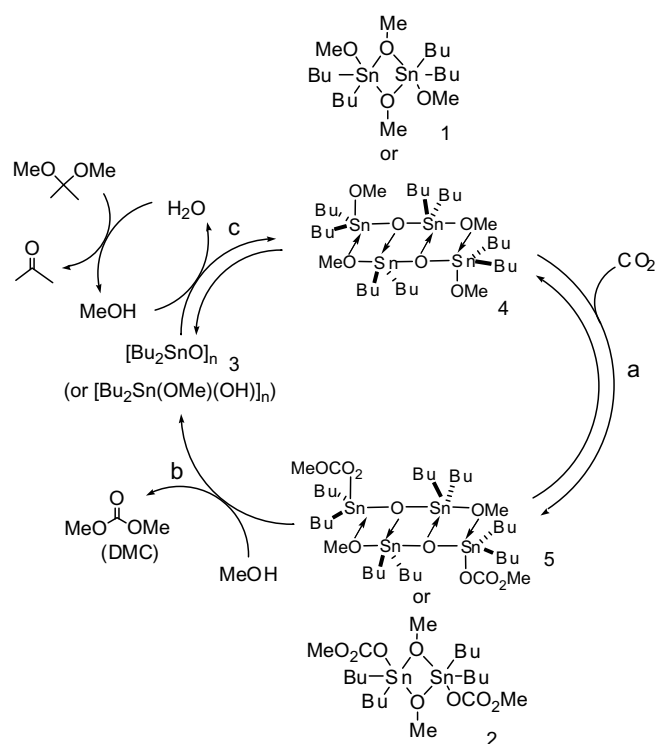
carbonate, and a subsequent ester exchange with methanol, and (4) direct dehydrative condensation of carbon dioxide with methanol (Eq. (1)) [8,9]. Although the last procedure (Eq. (1)) is the most attractive in view of green chemistry, this reaction is thermodynamically quite unfavorable. Another problem is deactivation of the catalyst by the co-produced water.

$$2\ MeOH\ +\ CO_2\ \rightleftharpoons\ MeO\overset{\displaystyle O}{\underset{}{\diagup\!\!\diagdown}}OMe\ +\ H_2O \tag{1}$$
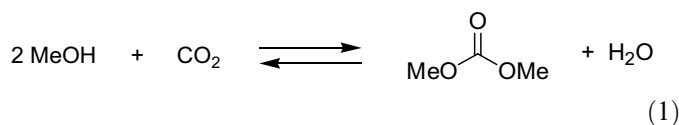
In order to circumvent these problems, we have already reported a $\{Bu_2Sn(OMe)_2\}_2$-catalyzed DMC synthesis starting from methanol and carbon dioxide in the presence of dimethyl ketals as a recyclable organic dehydrating agent [10–13]. A possible catalytic cycle has been postulated based on stoichiometric studies (Scheme 1); namely the conversion of **1** to **2** through CO_2 insertion (step a) [11,14], and DMC formation through methanolysis of

---

* Corresponding author. Tel./fax: +81 29 861 4719.
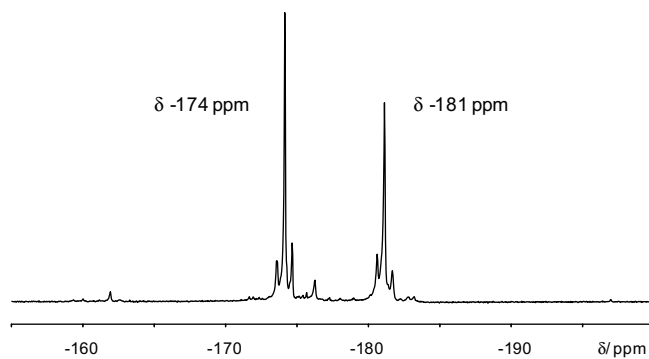 *E-mail address:* t-sakakura@aist.go.jp (T. Sakakura).

Scheme 1. Possible catalytic cycle of the Sn-catalyzed DMC synthesis.

Fig. 1. ^{119}Sn NMR spectrum of the reaction mixtures found in the Sn-catalyzed DMC synthesis.

stannoxane dimer **4** could be the real active intermediate in the catalytic cycle (see Scheme 1).
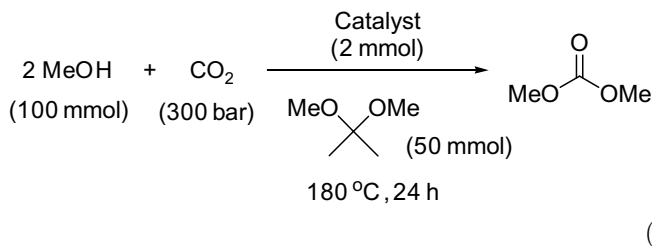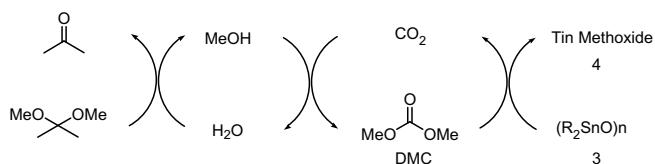

(2)

dinuclear carbonate complex **2** (step b) [11,14]. However, regeneration of tin methoxide such as $\{Bu_2Sn(OMe)_2\}_2$ (**1**) in the presence of dimethyl ketals (step c) has yet to be fully elucidated. Although the formation of tin methoxide from a tin oxide or hydroxide (step c, Scheme 1) has been investigated by several groups using various dehydrating procedures (e.g. azeotropic distillation [15], DMC addition [16], $Si(OMe)_4$ addition [17], and zeolite addition [18]), each procedure has limitations and is less practical than dehydration with dimethyl ketals. In this paper, we report the transformation of dibutyltin oxide $(Bu_2SnO)_n$ (**3**) to tin methoxide **4** in nearly quantitative yield. The transformation is promoted by a dimethyl ketal and a high CO_2 pressure.

2. Results and discussion

Elemental analysis showed that the end product in DMC formation by methanolysis of **2** (step b, Scheme 1) had a formula close to $(Bu_2SnO)_n$ (**3**) [17]. Hence, we investigated the transformation of $(Bu_2SnO)_n$ (**3**) using methanol under reaction conditions similar to those in catalytic DMC synthesis (300 bar of CO_2, 180 °C). After 24 h, the tin species in the reaction mixture was analyzed by ^{119}Sn NMR. The spectrum showed two different peaks in a one to one ratio (Fig. 1). Judging from Fig. 1, the major tin species in the reaction mixture was $\{Bu_2(MeO)Sn–O–Sn(O-Me)Bu_2\}_2$ (**4**) [15–17] rather than the dialkoxide, $\{Bu_2Sn(OMe)_2\}_2$ (**1**) [16]. Because the catalytic activity of **4** in the DMC synthesis is as high as alkoxide **1** (Eq. (2)),

In order to convert **3** to **4** in high yields, the presence of CO_2 is very important, as exhibited in Table 1. Although the conversion of **3** to **4** (step c, Scheme 1) occurred even in the absence of CO_2 (Runs 5–7, Table 1), the reaction was largely promoted by CO_2. Thus, the yield of stannoxane **4** was only 1% in the absence of CO_2 at 150 °C after 24 h (Run 7), but was 93% (Run 2) in the presence of CO_2 (60 bar). The acceleration by CO_2 pressure is presumably ascribed to the involvement of DMC as a mediator (Scheme 2).

The lower yield of **4** at 180 °C (Run 1, Table 1) compared to the yield at 150 °C (Run 2) under CO_2 is ascribed to the formation of by-products such as Bu_4Sn through disproportionation. Under CO_2 pressure, the conversion of **3**–**4** proceeded even at 100 °C (Run 4). It is noteworthy that this temperature is much lower than the temperature required for catalytic DMC synthesis [12,13,19]. Hence,

Table 1
Temperature and pressure effect on the conversion of $[Bu_2SnO]_n$ (**3**) to $\{Bu_2(MeO)Sn–O–Sn(OMe)Bu_2\}_2$ (**4**)

Run	Temperature (°C)	P_{CO_2} (bar)	Yield of **4** (%)
1	180	60	48
2	150	60	93
3	120	60	69
4	100	60	41
5	200	0	18
6	180	0	21
7	150	0	1

Reaction conditions: **3** (4 mmol), MeOH 100 mmol, 2,2-dimethoxypropane (24 mmol), 24 h.

Scheme 2. DMC-mediated conversion of tin oxides to tin methoxides.

Table 2
Effect of acetal amount on the conversion of $[Bu_2SnO]_n$ (3) to $\{Bu_2(MeO)Sn-O-Sn(OMe)Bu_2\}_2$ (4)

Acetal/Sn (mol/mol)	Yield of 4 (%)
0.5	5
1	86
3	95
6	93

Reaction conditions: 3 (4 mmol), MeOH 100 mmol, CO_2 (60 bar), 2,2-dimethoxypropane, 150 °C, 24 h.

Table 3
Effect of reaction time on the conversion of $[Bu_2SnO]_n$ (3) to $\{Bu_2(MeO)Sn-O-Sn(OMe)Bu_2\}_2$ (4)

Reaction time (h)	Yield of 4 (%)
1.5	70
2	88
3	91
6	99
24	95

Reaction conditions: 3 (4 mmol), MeOH 100 mmol, CO_2 (60 bar), 2,2-dimethoxypropane (12 mmol), 150 °C.

regeneration of tin methoxide is probably not the rate-determining step in the catalytic DMC synthesis (Scheme 1 and Table 1).

A more precise pressure effect in the lower pressure region (0–60 bar) was also investigated (Fig. 2). A low CO_2 pressure around 7 bar effectively achieved a conversion over 70%.

Table 2 summarizes the effect of the amount of acetal in the synthesis of 4. When the acetal/Sn ratio (mol/mol) was less than one, the yield of 4 was miserable due to the decomposition by water. One equivalent of acetal was sufficient to obtain 4 in over 85% yield. Employing 3 equiv. of acetal resulted in a nearly quantitative yield of 4. A few other groups have reported the formation of 4 from 3 [15]. However, we have found that the reaction is accelerated by the presence of acetal. The time course of the reaction at 150 °C revealed that the conversion of 3 to 4 was rather fast at this temperature (see Table 3). Although a 2 h reaction gave 4 in sufficient yield (88%), a 6 h reaction resulted in a nearly quantitative yield.

In summary, we have developed an efficient synthesis of stannoxane dimer (4) by the reaction of dibutyltin oxide (3) and methanol in the presence of 2,2-dimethoxypropane under CO_2. A high pressure CO_2, an excess of 2,2-dimethoxypropane, and a longer reaction time are preferable for promoting the formation of stannoxane (4). Because the conversion of 3 to 4 proceeds under relatively mild conditions (even at 100 °C), stannoxane dimer 4 rather than 1 could be the active intermediate in the real catalytic cycle.
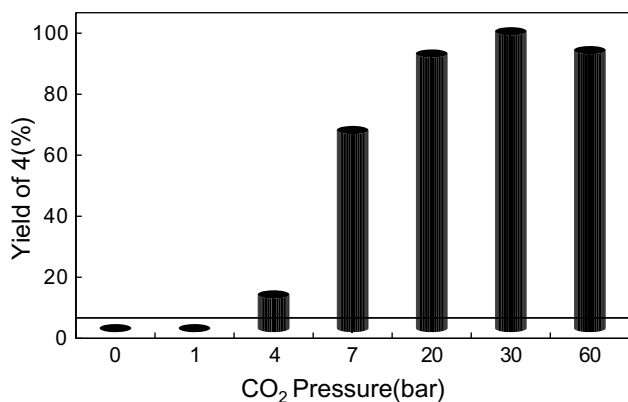
3. Experimental

3.1. General procedures

All manipulations were conducted under purified argon or nitrogen. 2,2-Dimethoxypropane, $Bu_2Sn(OCH_3)_2$ (1), Bu_2SnO (3) and Et_4Sn were purchased from Aldrich Co. Carbon dioxide (Showa Tansan Co., Kawasaki, purity >99.99%) was used without further purification. The standard compound $\{Bu_2(MeO)Sn-O-Sn(OMe)Bu_2\}_2$ (4) was synthesized from an equimolar mixture of $Bu_2Sn(OCH_3)_2$ (1) and Bu_2SnO (3) according to the literature method [17]. Reaction products were analyzed by NMR and GC–MS. ^1H, ^{13}C and ^{119}Sn NMR spectra were measured on a JEOL LA-400WB superconducting high-resolution spectrometer (400 MHz for ^1H). ^{119}Sn $\{^1H\}$ NMR spectra were referenced to external Et_4Sn. GC analysis was conducted using capillary columns; GL Science TC-1 (60 m) on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID). All the volatile products were also characterized with GC–MS using a Shimadzu GC-17A gas chromatograph connected to a GCMS-QP 5000 mass spectrometer.

3.2. Typical reaction procedure

In a stainless steel autoclave (20 cm^3 inner volume), carbon dioxide (20 bar) was added to a mixture of methanol (100 mmol), Bu_2SnO (3) (4 mmol), and 2,2-dimethoxypropane (12 mmol) at room temperature. The initial pressure was adjusted to 60 bar at 150 °C, and the autoclave was heated at that temperature for 6 h. After cooling to room temperature, the solvent was removed under vacuum. The Et_4Sn (10 mg) was added to the solution of the

Fig. 2. Pressure effect on the conversion of $[Bu_2SnO]_n$ (3) to $\{Bu_2(MeO)Sn-O-Sn(OMe)Bu_2\}_2$ (4). Reaction conditions: 3 (4 mmol), MeOH 100 mmol, 2,2-dimethoxypropane (12 mmol), 150 °C, 3 h.

reaction product in CDCl$_3$ as the internal standard in order to determine product yield by NMR.

3.3. Catalytic reaction procedures

In a stainless steel autoclave (20 cm^3 inner volume), carbon dioxide (liquid, 65 bar) was added to a mixture of methanol (100 mmol), **4** (2 mmol), and 2,2-dimethoxypropane (50 mmol) at room temperature. The initial pressure was adjusted to 300 bar at 180 °C, and the autoclave was heated at that temperature for 24 h. After cooling, 1,3,5-trimethylbenzene (100 µL) was added to the reaction mixture as the internal standard for the GC analysis.

References

[1] M.A. Pacheco, C.L. Marshall, Energy Fuels 11 (1997) 2.
[2] P. Tundo, M. Selva, S. Memoli, ACS Symp. Ser. 767 (2000) 87.
[3] P. Tundo, M. Selva, Acc. Chem. Res. 35 (2002) 706.
[4] A.A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[5] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, Green Chem. 5 (2003) 497.
[6] T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
[7] Y. Sato, M. Kagotani, T. Yamamoto, Y. Souma, Appl. Catal. A 185 (1999) 219.
[8] M. Aresta, M. Galatola, J. Clean. Prod. 7 (1999) 181.
[9] M. Aresta, A. Dibenedetto, I. Tommasi, Energy Fuels 15 (2001) 269.
[10] T. Sakakura, Y. Saito, M. Okano, J.-C. Choi, T. Sako, J. Org. Chem. 63 (1998) 7095.
[11] J.-C. Choi, T. Sakakura, T. Sako, J. Am. Chem. Soc. 121 (1999) 3793.
[12] T. Sakakura, J.-C. Choi, P. Saito, T. Masuda, T. Sako, T. Oriyama, J. Org. Chem. 64 (1999) 4506.
[13] T. Sakakura, J.-C. Choi, Y. Saito, T. Sako, Polyhedron 19 (2000) 573.
[14] D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, Organometallics 19 (2000) 4563.
[15] A.G. Davies, D.C. Kleinschmidt, P.R. Palan, S.C. Vasishtha, J. Chem. Soc. C (1971) 3972.
[16] E.N. Suciu, B. Kuhlmann, G.A. Knudsen, R.C. Michaelson, J. Organomet. Chem. 556 (1998) 41.
[17] D. Ballivet-Tkatchenko, T. Jerphagnon, R. Ligabue, L. Plasseraud, D. Poinsot, Appl. Catal. A 255 (2003) 93.
[18] J.-C. Choi, T. Sakakura, T. Sako, AIST, Japan patent 3385359, 2003.
[19] J.-C. Choi, L.N. He, H. Yasuda, T. Sakakura, Green Chem. 4 (2002) 230.