

PREPARATION OF DIMETHYL CARBONATE FROM METHANOL AND CARBON DIOXIDE IN THE PRESENCE OF Sn(IV) and Ti(IV) ALKOXIDES AND METAL ACETATES

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The synthesis of dimethyl carbonate by the reaction of methanol with carbon dioxide in the presence of metal alkoxides and metal carboxylates was studied. The best results have been achieved with Ti(IV) and Sn(IV) alkoxides which at 130 to 180 °C and low CO₂ pressures yield dimethyl carbonate in 30 to 100 mole % or 40 to 130 mole % yields with respect to the metal alkoxides, depending on the carbon dioxide (gaseous and solid one, respectively). The yields can be further increased up to 70 – 190 mole % and 90 – 270 mole %, respectively, by the use of chemical scavengers of the reaction water.

Dimethyl carbonate is an important methylating agent which replaces former toxic methylating agents, and also an intermediate of synthesis of higher carbonates and fuel additive. It is produced industrially by carbonylation of methanol in the presence of copper or palladium catalysts¹.

An alternative route is the reaction of carbon dioxide with methanol in the presence of organotin compounds, especially dialkyltin dialkoxides², as well as the use of Sn(IV), Ti(IV) or Zr(IV) alkoxides^{3,4}. In our previous studies we reported on the activity of other organotin compounds, using both solid⁵ and gaseous⁶ carbon dioxide. We attempted at improving reaction conditions and product yields compared to the other authors²⁻⁴, which, however, has been achieved only in the presence of chemical scavengers of the reaction water⁶. This led us to examine further the activity of metal(IV) alkoxides and metal carboxylates in this process which is not a typical catalytic reaction⁵. The effectiveness of metal alkoxides for similar types of reactions was already generally surveyed⁷. Of interest is also the use of mercury(II) acetate for synthesis of dialkyl carbonates, even though the preparation of dimethyl carbonate has not been specified⁸. In fact, many metal compounds of variable valence might be suitable agents in this reaction. Unfortunately, the presence of reaction water reduces markedly their effectiveness¹².

EXPERIMENTAL

Chemicals

Dimethyl carbonate, 99% purity (Aldrich). Methanol (analytical grade purity, 99.8% and 0.2% H₂O, Lachema Brno) was dried over sodium sulfate and calcium hydride and distilled through a column filled with sodium, yielding the product containing max. 0.01% H₂O. Tin(IV) ethoxide was obtained⁹ as a white hygroscopic powder, titanium(IV) methoxide was prepared by reesterification of Ti(IV) butoxide with methanol^{10,11} as a yellow powder melting at 202 °C. Titanium(IV) ethoxide was prepared similarly^{10,11} and obtained as a yellow liquid boiling at 130 – 133 °C/400 Pa. Titanium(IV) butoxide, a light brown liquid with b.p. 155 – 158 °C/400 Pa, was prepared by esterification of TiCl₄ as reported¹⁰. Dicyclohexylcarbodiimide (DCC) and trimethyl phosphate (TMP) (both chemical purity grade, min. 99%, Aldrich) were used as chemical scavengers of water. The other chemicals were of analytical purity. Carbon dioxide was either the dry ice (water content max. 2.0%) or gaseous carbon dioxide (pure, min. 98.5%, max. 0.5% H₂O, Tatragas Sala, The Slovak Republic).

Procedure

Solid carbon dioxide. A cooled 250 ml-stainless steel autoclave with frictional magnetic stirring and electrical heating⁵ was charged with 150 ml (120 g, 3.8 mol) of cold methanol, a metal(IV) alkoxide (10 mmol) and drying agent (10 g), followed by an initiator (5 mmol) and/or a water scavenger (50 mmol). Then, a total of 44 g (1.0 mol) of dry ice were portionwise added. The autoclave was closed and its contents were heated to 150 °C for 6 to 12 h. The cooled reaction mixture was filtered and analyzed by GLC. The results of these experiments are presented in Table I.

Gaseous carbon dioxide. A 150 ml-stainless steel autoclave equipped with magnetic stirring and immersed in an electrically heated silicone bath⁶ was charged with 40 ml (30 g, 1.0 mol) of methanol, a metal(IV) alkoxide (10 mmol), a drying agent (8 g) and eventually also with an initiator (5 mmol) and/or a water scavenger (50 mmol). The reactor was closed, purged and then pressured with gaseous carbon dioxide and heated to 150 °C for 20 h. The reaction mixture was worked up as described in the preceding paragraph. The results obtained are summarized in Table II.

Analyses

GLC analyses were carried out on a Chrom-4 gas chromatograph equipped with CI-100 integrator (Laboratorni pristroje, Prague) under the following conditions: FID detector, 2 m column (4 mm i.d.) packed with 10% silicone elastomer SE 30 on Chromaton N-AW-DMCS (0.100 – 0.125 mm), column temperature 60 °C, injection port temperature 200 °C (other suitable packings were found to be SE-31, SE-301 or Reoplex-400), nitrogen as a carrier gas. Toluene was used as an internal reference. The relative error of the GLC analysis was ±3 per cent.

RESULTS AND DISCUSSION

The results presented in Tables I and II document that the best metal compounds for the title reaction are tin(IV) or titanium(IV) alkoxides, especially butoxides. It seems likely that mechanism of the reaction is the same as in the presence of previously studied organotin compounds^{4,5}. These afforded dimethyl carbonate in up to 260 mole % yields⁴, and with the use of chemical scavengers of reaction water even in up to 330 mole % yields⁶, most likely as the result of the better stability of the above tin com-

TABLE I

Activity of metal(IV) alkoxides (10 mmol) in the reaction of solid carbon dioxide (1.0 mol) with methanol (3.8 mol) in the presence of initiators (NaCl or Hg(OAc)₂ 5 mmol) and/or chemical scavengers of reaction water (TMP or DCC, 50 mmol) at 150 °C (total pressure 6 MPa, reaction time 6 h)

Metal (IV) alkoxide	Addend ^a	Yield, %		
		EtOH	AcOMe ^b	(MeO) ₂ CO ^c
Sn(OEt) ₄	none	60	0	86
	none (200 °C)	85	0	111
	NaBr	68	0	82
	Hg(OAc) ₂	62	37	88
	TMP	67	0	105
	DCC	62	0	125
	Hg(OAc) ₂ + TMP	63	54	122
	NaBr + DCC	60	0	185
Ti(OMe) ₄	none	0	0	33
	none (200 °C)	0	0	58
	NaBr	0	0	53
	Hg(OAc) ₂	0	44	48
	Hg(OAc) ₂ + TMP	0	42	75
	NaBr + DCC	0	0	88
Ti(OEt) ₄	none	66	0	50
	NaBr	68	0	55
	Hg(OAc) ₂	65	35	55
	Hg(OAc) ₂ + TMP	70	38	103
	NaBr + DCC	70	0	147
Ti(OBu) ₄	none	67 ^d	0	75
	none (200 °C)	85 ^d	0	105
	NaBr	64 ^d	0	76
	Hg(OAc) ₂	66 ^d	0	78
	TMP	63 ^d	0	90
	DCC	65 ^d	0	108
	Hg(OAc) ₂ + TMP	68 ^d	43	113
	Hg(OAc) ₂ + TMP (200 °C)	84 ^d	58	137
	NaBr + DCC	70 ^d	0	175
	NaBr + DCC (200 °C)	80 ^d	0	190

^a TMP trimethyl phosphate, DCC dicyclohexylcarbodiimide. ^b Expressed as mole % per mole of the addend. ^c Calculated as mole % per mole of metal(IV) alkoxide. ^d The yield of butanol.

TABLE II

Activity of metal(IV) alkoxides (10 mmol) in the reaction of gaseous carbon dioxide (total pressure 2.5 MPa) with methanol (1 mol) in the presence of initiators (NaBr or Hg(OAc)₂, 5 mmol) and/or chemical scavengers of reaction water (TMP or DCC, 50 mmol) at 150 °C (reaction time 20 h)

Metal(IV) alkoxide	Addend ^a	Yield, %		
		EtOH	AcOMe ^b	(MeO) ₂ CO ^c
Sn(OEt) ₄	none	80	0	150
	none (180 °C)	93	0	163
	NaBr	80	0	160
	Hg(OAc) ₂	80	48	156
	TMP	80	0	166
	DCC	80	0	220
	Hg(OAc) ₂ + TMP	83	60	175
	NaBr + DCC	86	0	233
Ti(OMe) ₄	none	0	0	40
	none (200 °C)	0	0	68
	NaBr	0	0	48
	Hg(OAc) ₂	0	55	48
	Hg(OAc) ₂ + TMP	0	50	94
	NaBr + DCC	0	0	111
Ti(OEt) ₄	none	82	0	63
	none (180 °C)	90	0	126
	Hg(OAc) ₂ + TMP	77	53	123
	NaBr + DCC	70	0	183
Ti(OBu) ₄	none	80 ^d	0	105
	none (180 °C)	100 ^d	0	140
	NaBr	85 ^d	0	122
	Hg(OAc) ₂	88 ^d	55	133
	TMP	88	0	144
	DCC	80	0	200
	Hg(OAc) ₂ + TMP	95	83	165
	Hg(OAc) ₂ + TMP (180 °C)	100	85	188
	NaBr + DCC	90	0	237
	NaBr + DCC (180 °C)	100	0	268

^a TMP trimethyl phosphate, DCC dicyclohexylcarbodiimide. ^b Expressed as mole % per mole of the addend. ^c Calculated as mole % per mole of metal(IV) alkoxide. ^d The yield of butanol.

pounds. The previously used initiators^{5,6} such iodine, methyl iodide, mercury(II) iodide and others turned out to be less suitable in the present case because of their promoting effect on metal tetraalkoxide decomposition. The better agents are heavy metal (especially Hg) acetates or alkali metal halides such as NaBr, NaI etc. which cause a partial metal tetraalkoxide decomposition mainly at higher temperatures¹².

One can conclude that the reproducibility of the results of earlier studies²⁻⁴ is only partial or nearly none (the yields of the carbonate did not exceed 20 mole % in the case of metal acetates (Mn, Co, Sn, and Zn) as such, and 30 mole % with the use of the mercury salt). The heavy metal acetates thus do not promote dimethyl carbonate production but they undergo mostly decomposition, this being accompanied by the esterification of acetic acid to methyl acetate. In the absence of water scavengers, the yields of dimethyl carbonate did not exceed 160 mole % with respect to the metal(IV) alkoxide, because of the already mentioned negative effect of the reaction water. The higher temperature up to 200 °C facilitates the reaction⁵ but this trend is not in all cases so straightforward. Thus for example, at temperatures above 150 °C, the efficiency of tin(IV) ethoxide does not further increase. It is supposed that the higher temperature shows favourable effect on both the cleavage of the reaction intermediate to give dimethyl carbonate and on the subsequent conversion of metal(IV) alkoxide to the metal metoxide⁵. It is of interest that titanium(IV) methoxide is the less efficient agent compared to the higher alkoxides, although the latter are transformed into the former by reesterification with methanol during the studied carbonylation reaction. The use of a drying agent turned out to be advantageous, the best one being MgSO₄, the less suitable agents then Na₂SO₄ and molecular sieves (Nalsit, Calsit and Potasit). The determination of the water content in the reaction mixture after the reaction by Fisher method showed that the inorganic drying agents ensure in average max. 0.02%, the chemical scavengers such as trimethyl phosphate (TMP) max. 0.013% and dicyclohexylcarbodiimide (DCC) so low as max. 0.003%. These data provide evidence for the decisive negative effect of the reaction water on the yields of the reaction. The yields of dimethyl carbonate obtained (70 – 270 mole %) are comparable to those reported in previous works²⁻⁴ (260 mole %), and in some respect even somewhat better as they were achieved after shorter (ca by 4 h) reaction times. Nevertheless, because of the lower stability of metal(IV) alkoxides, the dialkyltin(II) compounds studied earlier⁶ are the more convenient agents for this purpose since they afford dimethyl carbonate in more than 300 mole per cent yields.

REFERENCES

1. Romano U., Tesei R., Masuri M. M., Rebora F.: *Ind. Eng. Chem., Prod. Res. Dev.* **19**, 396 (1980).
2. Sakai S., Fujinami T., Furusawa S.: *Nippon Kagaku Kaishi* **10**, 1789 (1975); *Chem. Abstr.* **84**, 5090 (1976).

3. Yamazaki N., Nakahama S., Endo K. (Mitsubishi Co.): Japan. Kokai 79 3,012; Chem. Abstr. 90, 168087 (1979).
4. Yamazaki N., Nakahama S.: Ind. Eng. Chem., Prod. Res. Dev. 18, 249 (1979).
5. Kizlink J.: Collect. Czech. Chem. Commun. 58, 1399 (1993).
6. Kizlink J., Pastucha I.: Collect. Czech. Chem. Commun. 59, 2116 (1994).
7. Bradley D. C.: Prog. Inorg. Chem. 2, 303 (1960).
8. Ota H. (Mitsai Toatsu): Japan 70 24,966; Chem. Abstr. 73, 98378 (1970).
9. Bradley D. C., Caldwell E. V., Wardlaw W.: J. Chem. Soc. 1957, 4775.
10. Bischoff F., Adkins H.: J. Am. Chem. Soc. 46, 256 (1924).
11. Bradley D. C., Hancock D. C., Wardlaw W.: J. Chem. Soc. 1952, 2773.
12. Sheldon R. A., Kochi J. K.: *Metal-Catalyzed Oxidations of Organic Compounds*. Academic Press, New York 1981.