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High Pressure Routes to Dimethyl Carbonate from Supercritical Carbon Dioxide

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Abstract: A technique for the application of high pressure conditions to reactions carried out in supercritical carbon dioxide is reported. The effect of high pressure and the conditions for the formation of dimethyl carbonate from carbon dioxide by three routes has been examined.

Keywords; dimethyl carbonate, high pressure, carbon dioxide

Industrially important derivatives of carbonic acid include dialkyl carbonates used as solvents[1], alkylating agents, fuel additives and in the synthesis of polycarbonate resins. These, on an industrial scale are usually prepared from phosgene[2]. Its use, however, has serious disadvantages which include intense toxicity. It is an expensive intermediate in that its preparation is from high energy reagents typically chlorine and carbon monoxide. Products include chloride ion which represents wasted energy and gives disposal problems involving neutralization by sodium hydroxide. On a large scale, corrosion of equipment is serious. Other viable routes to dimethyl carbonate include the oxidative carbonylation of methanol requiring copper-(II) or palladium-(II) [3-9] which is expensive in using CO and accompanied by a potential explosion hazard. Direct esterification of methanol by carbon dioxide has been reported over a zirconium oxide catalyst [10] while transesterification methods may be applied to obtain, for example dimethyl carbonate from the more easily prepared cyclic esters[11-13] and from amides.[14] Finally, insertion of CO_2 into a metal-alkoxy bond followed by methylation has been shown to be feasible[14].

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The present work explores the use of carbon dioxide, a readily available, inexpensive and environmentally acceptable starting material, as a source of a single carbon unit for the formation of dimethyl carbonate by three different routes. All of these methods are associative processes which should be facilitated by high pressures (1000 MPa) and the effectiveness of this parameter is examined.

In general, carbonate esters could arise from CO_2 by the addition of elements supplying nucleophilic alkoxide and electrophilic alkyl cation.

Synthetic routes described below explore different sources of these components and their reactivities

Apparatus and methods

Reactions using liquid or supercritical carbon dioxide at pressures up to about 300 bar were conducted in a Whitey cylinder of 50 mL capacity fitted with a 400 MPa miniature valve (Nova Swiss) and gas delivery tube. Solid and liquid reagents were weighed directly into the cylinder with the valve removed. After replacing this, carbon dioxide was admitted at a pressure above that of the liquid using a gas booster (Haskell) until the requisite weight was present. The valve was then closed, the cylinder detached and held at the required temperature in an oven. Depressurization occurred on cooling and opening the valve.

Samples which were to be taken to high pressures (900-1000 MPa) were prepared in the following apparatus, Fig.1. A stainless steel cylinder (a) was fitted with an internal ring (c) at one end, a piston with O-rings (b) and a non-return valve (d) at the other. With the valve detached, liquid and solid samples were admitted. The valve was replaced and the required amount of carbon dioxide admitted at about 100 bar through the check valve using a gas booster pump. The cylinder and valve were detached from the gas supply, the inlet side capped (e) to prevent high pressure oil entering through the valve and the whole unit placed in a high pressure apparatus described previously in which, immersed in oil, it could be subjected to hydrostatic pressure up to 1000 MPa and the desired temperature. This pressure was transmitted to the sample inside the

cylinder by the movable piston. Depressurisation was achieved by cooling the cylinder and gently releasing the non-return valve from its seating.

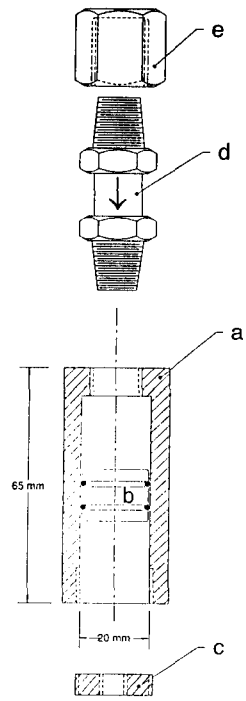


Fig.1; apparatus for using supercritical carbon dioxide at high pressure

Results

1. Dimethyl carbonate from orthoester and a dimethoxystannane catalyst

In a typical experiment, the following materials were charged into the reaction vessel , either the Whitey cylinder or the high pressure vessel; trimethyl orthoacetate (TMO), (6.0g, 50 mmol), tetrabutylammonium iodide, (0.33g, 0.8 mmol) or methyl iodide (0.5-1.5 g, 3-10 mmol) and dibutyldimethoxystannane (0.27g, 1.1 mmol) together with anisole (0.1g) to act as a g.l.c. reference. Liquid carbon dioxide (5-6g, 110-140 mmol)

was pumped in and the vessel sealed and heated or pressurized for the appropriate period (6-48h). After cooling, the vessel was opened and the contents analysed by g.l.c. A representative selection of analytical data is shown in Table 1.

Table 1; DMC formation from trimethyl orthoacetate and tin catalyst

Run No.	t/h	p/MPa	T/°C	TMO / Mmol	$R_4N^+I^-$ /mmol	MeI /mmol	$R_2Sn(OR)_2$ /mmol	CO_2 \mmol	% DMC
1	72	30	120	50	0.8		1.2	100	15
2	48	30	150	50	0.8		1.2	120	30
3	40	940	65	25	1.0		1.2	110	12
4	20	910	75	25	1.1		1.2	110	13
5	20	940	75	25	1.1	3.0	1.2	110	38
6	20	920	60	12	1.1	3.0	1.2	110	38
7	6	900	70	0	1.2	3.0	1.2	110	28
8	6	910	70	0	0	6.4	0	110	0

2. Dimethyl carbonate by base-catalysed addition of methanol and methyl iodide to CO_2

The following reagents were charged into the high pressure cylinder described above; methanol (3.1g,100 mmol), anhydrous potassium carbonate (0.2g, 1.4 mmol) and methyl iodide (1.7 - 3.4 g , 12-24 mmol). Carbon dioxide (5-6 g) was pumped in and the apparatus sealed and pressurized at 900-1000 MPa. After depressurization, the contents were analysed by g.l.c. A representative selection of analytical data is presented in Table 2

Table 2; DMC formation from methanol and methyl iodide

No.	t/h	T / °C	MeOH/ Mmol	K_2CO_3 / mmol	MeI / mmol	MeI used /mmol	% DMC[3]
1	20	60	100	1.5	12	5	130
2	3	60	100	1.5	12	2	80
3	20	60	100	3.0	12	7.8	110
4	20	60	100	1.5	25	7.7	100
5 [1]	20	60	100	1.5	12	4	90
6	20	100	100	1.5	12	5	100
7 [2]	20	60	100	1.5	12	4.5	90

[1] carried out at 120 bar : [2] in the presence of 2Å molecular sieves
[3] based on moles of K_2CO_3 used as catalyst

3. By esterification of methanol in the presence of DCC

The following reagents were loaded into the Whitey cylinder; methanol, (1.0g, 31 mmol), dicyclohexylcarbodiimide (DCC), (6.5g, 31 mmol) , anisole as g.l.c. reference (1.0 g) . Carbon dioxide (approx 7g, 160 mmol) was admitted at 120 bar , the cylinder sealed and agitated to dissolve the contents after which it was heated in an oven at 50°C for 6 h. Products were removed and analysed by g.l.c.

The product contained solid dicyclohexylurea from which was extracted volatile products with ether. The ethereal solution was examined by glc and found to contain no methanol but a quantitative yield of dimethyl carbonate.

An analogous reaction was carried out using ethanol in place of methanol. After 3 h, the product contained only a trace of diethyl carbonate and a time of around 18 h at 70° was required in order to effect complete conversion.

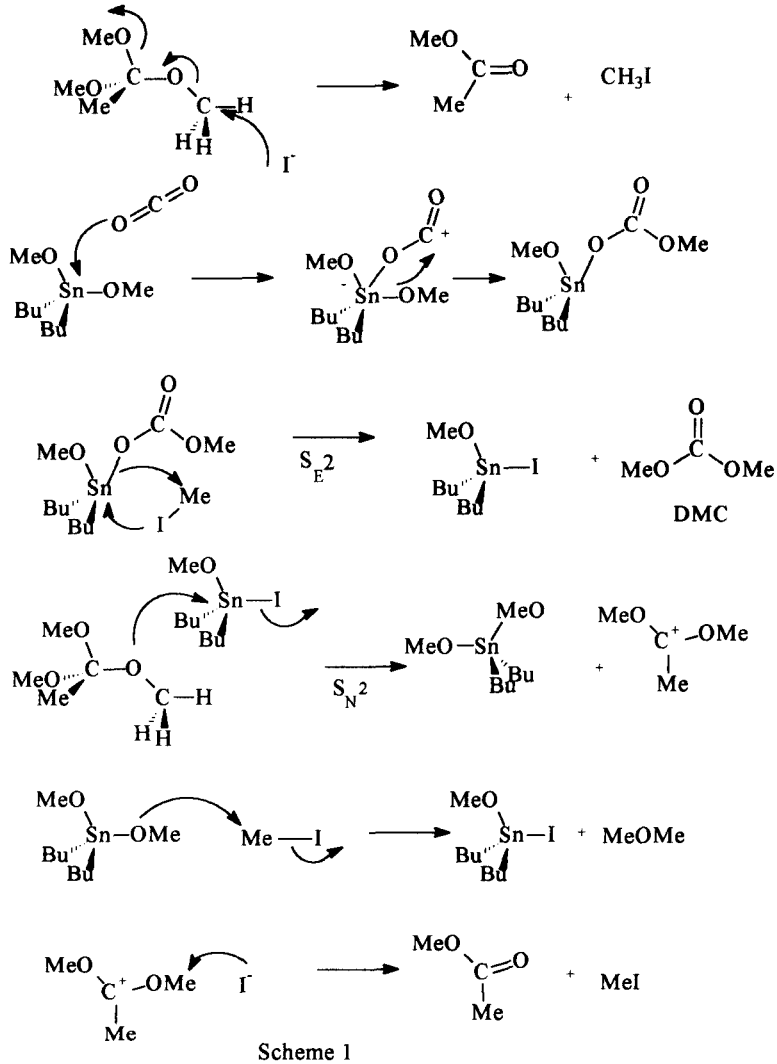
Discussion

None of the reactions carried out were optimized but serve to indicate the potential of the methods used.

Method 1 using trimethyl orthoacetate and a dimethoxytin catalyst described by Sakekura[15,16] occurs by a chain reaction in which the methylating reagent is methyl iodide generated by the action of iodide on the orthoacetate, Scheme 1.

When not separately added, methyl iodide was detected in the reacting system by g.l.c. and the yield of DMC was found to be improved if this compound was actually added among the reagents to methylate the carbonate ligand formed from insertion of carbon dioxide into the Sn-O bond. It is likely that the catalyst becomes deactivated through the eventual formation of inert tin iodide complexes which limits the yield.

High pressure was found to be beneficial. Under CO_2 pressure alone, no product was formed at 70°C. In fact, a temperature of at least 150°C was needed in the absence of high pressure to give any DMC at all and then at no better yield. At 900 MPa and temperatures in the 60-70°C range, yields of 38% could be obtained.



Scheme 1

Direct esterification catalysed by potassium carbonate was found to occur but conditions are necessarily heterogeneous and this method suffers from the insolubility of the catalyst which also is required to remove water. Yields were improved by increasing the amount of base already above a stoicheometric amount. Reactions were carried out at 1000 MPa or under CO_2 pressure (about 20 MPa) but surprisingly, the yields were not greatly affected by pressure although an approximate calculation from molar volumes suggests the volume of reaction to be about -20 cm^3mol^{-1}. It seems likely that

conditions were not those in which equilibrium could be established. A raise in the temperature to 100°C did significantly improve the yield. The limitation here may be the weakness of the base used (CO_3^{2-}) since any stronger bases might have coordinated to the carbon dioxide . Further measurements are being made to explore the possibility of stronger or more soluble bases since this route is sufficiently promising that it might be explored further for large scale application.

Esterification of CO_2 by methanol is found to be promoted by carbodiimide though this route does not seem to have been mentioned previously . It gave essentially quantitative formation of dimethyl carbonate under mild conditions but was less effective in the formation of the corresponding ethyl ester and this presumably would be the case with higher alcohols. This reaction could have laboratory application in view of the mild conditions used. Further exploration of this reaction is being undertaken, particularly the effectiveness of high pressure in promoting reaction with higher alcohols.

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