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THE REACTION OF METHOXY KETALS AND DIMETHYL CARBONATE WITH SYNTHESIS GAS

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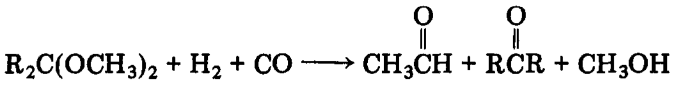
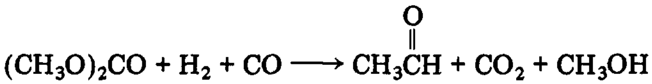
Summary

The reaction of dimethoxy ketals and dimethyl carbonate with synthesis gas results in the formation of acetaldehyde.



$$R_2C(OCH_3)_2 + H_2 + CO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + R\overset{O}{\overset{\|}{C}}R + CH_3OH$$

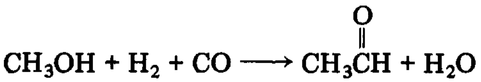


$$(CH_3O)_2CO + H_2 + CO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + CO_2 + CH_3OH$$

In the case of methoxy ketals, the reaction is carried out with a cobalt catalyst at 130 °C and 2500 psi. The rate of acetaldehyde formation is 4.0 M h^{-1}. The reaction of dimethyl carbonate requires a cobalt–iodide catalyst and operating conditions of 180 °C and 4000 psi. In this case, the rate of formation of acetaldehyde approaches 30 M h^{-1}. Mechanisms are discussed which are consistent with results obtained from high pressure infrared studies and stoichiometric model reactions.

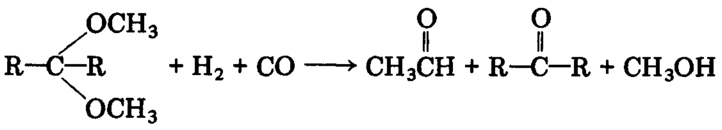
Introduction

In conjunction with our work dealing with the reductive carbonylation of methanol, eqn. (1),



$$CH_3OH + H_2 + CO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + H_2O \qquad (1)$$

we have studied the reactions of methyl ketals with synthesis gas [1]. In the presence of a cobalt-based catalyst, acetaldehyde is obtained according to eqn. (2).



(2)

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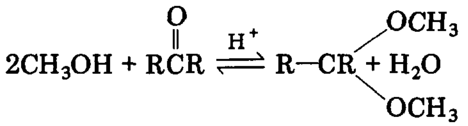
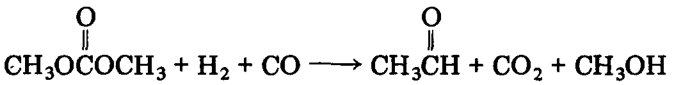
The co-produced ketone and methanol can be recycled via the equilibrium represented by eqn. (3) [2].



$$\mathrm{2CH_3OH + R\overset{O}{\overset{\|}{C}}R \xrightleftharpoons{H^+} R{-}CR(OCH_3)_2 + H_2O} \qquad (3)$$

Combination of eqns. (2) and (3) yields eqn. (1). The advantage of utilizing a methyl ketal feedstock is that reaction (2) can be carried out at high productivity under relatively mild operating conditions: 135 °C and 2500 psi compared to 170 - 190 °C and 3000 - 6000 psi for the reductive carbonylation of methanol [3 - 7].

Additionally, we have found that dimethyl carbonate reacts with synthesis gas to yield acetaldehyde:



$$\mathrm{CH_3O\overset{O}{\overset{\|}{C}}OCH_3 + H_2 + CO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + CO_2 + CH_3OH} \qquad (4)$$

This reaction is carried out at increased pressure, 3500 - 5000 psi, however the reaction rate is exceptionally high. To our knowledge, the use of dimethyl carbonate as a substrate in synthesis gas reactions has not been previously reported [8].

This paper details the reaction of methyl ketals and dimethyl carbonate with synthesis gas. The similarities and differences between the synthesis gas chemistry of methyl ketals, dimethyl carbonate and methanol will be explored with emphasis on the catalyst used, possible mechanisms and the general utility of the chemistry.

Experimental

The high-pressure reactions were carried out in a magnetically stirred 300 cm^3 autoclave of Hastelloy C construction. In a typical experiment $Co(OAc)_2 \cdot 4H_2O$ (12.0 mmol) and 150 ml 2,2-dimethoxypropane or $Co(OAc)_2 \cdot 4H_2O$ (12.0 mmol), CoI_2 (23.0 mmol), LiI (24.0 mmol) and 150 ml dimethyl carbonate are charged under N_2 to the clean reactor. The reactor is sealed and a H_2/CO (1:1) gas mixture is added to a pressure of ~500 psi. Agitation (750 rpm) is begun and the reactor is heated to the desired temperature within 40 min. At reaction temperature, the reactor is pressurized at 250 psi over the desired pressure. The reaction is allowed to consume 500 psi and then the reactor is repressurized. This process is repeated until the reaction ceases or is halted (typically after 3000 - 5000 psi consumption). The reactor contents are cooled via internal cooling coils with an H_2O/glycol mixture to 10 °C. A vapor phase sample is taken for analysis, a gas sample taken, and the liquid contents are collected in a chilled bottle.

Gaseous products were analyzed on a Carle chromatograph. The liquid products were analyzed with a Hewlett-Packard III-H Model 5880 gas chromatograph equipped with a 20 ft × 1/8 in 60/80 mesh Chromosorb 101 column. Methyl Cellosolve® was the internal standard. The following program was utilized: initial temperature = 80 °C, 6 °C min^{-1} increase for 12 min followed by 8.0 °C min^{-1} increase up to a final temperature of 290 °C.

The acetaldehyde rates are expressed as $M\ h^{-1}$ (moles per liter per hour) and are based on liquid volume. The acetaldehyde selectivity is calculated via

$$\text{AcH Selectivity} = \frac{\text{moles AcH} + \text{moles DMA}}{\text{total moles products}} \times 100\%$$

where AcH = acetaldehyde and DMA = 1,1-dimethoxyethane.

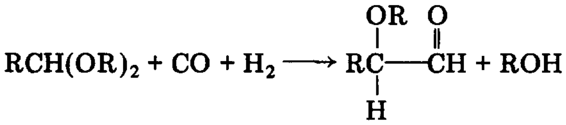
A description of the high-pressure IR equipment including the high-pressure IR cell and spectrometer, together with the usual operating procedure, has already appeared [9].

In the reaction of $HCo(CO)_4$ with 2,2-dimethoxypropane, $HCo(CO)_4$, prepared by a known procedure [10], was condensed into 50 ml of 2,2-dimethoxypropane (−77 °C) giving a 0.02 M solution. The mixture was warmed to 25 °C and maintained at 1 atm CO and 25 °C. After 12 h, all the $HCo(CO)_4$ had been converted to $Co_2(CO)_8$, as judged from changes in the IR spectrum [11]. Analysis of the liquid products by NMR and gas chromatography indicated the formation of methanol, 1,1-dimethoxyethane, acetaldehyde and acetone. The approximate molar ratio of methanol: acetaldehyde:acetone, including methanol and acetaldehyde equivalents in 1,1-dimethoxyethane, equaled 1:1:1.

Results and discussion

Non-halide catalysts

Aliphatic acetals yield 2-alkoxyaldehydes via cobalt-catalyzed reaction with synthesis gas [8, 12]:

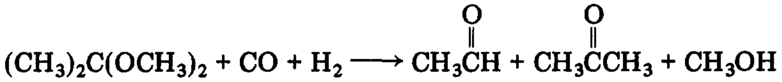


$$RCH(OR)_2 + CO + H_2 \longrightarrow R\overset{\displaystyle OR}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}H + ROH \qquad (5)$$

In contrast, acetals of aromatic aldehydes are not carbonylated but only undergo reductive cleavage [13].

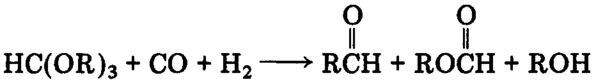
$$PhCH(OR)_2 + H_2 \longrightarrow PhCH_2OR + ROH \qquad (6)$$

We have found that methyl ketals react with synthesis gas in the presence of a cobalt catalyst to yield acetaldehyde, a ketone and methanol. For example, in the case of 2,2-dimethoxypropane the reaction proceeds according to eqn. (7).

 (7)

$$(CH_3)_2C(OCH_3)_2 + CO + H_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3OH \qquad (7)$$

A similar reaction is known for orthoformates [14 - 16].

 (8)

$$HC(OR)_3 + CO + H_2 \longrightarrow R\overset{O}{\overset{\|}{C}}H + RO\overset{O}{\overset{\|}{C}}H + ROH \qquad (8)$$

However, unlike methyl ketals, orthoformates are not readily regenerated by recycle of the alkyl formate and alcohol. Orthoformates are generally synthesized according to eqns. (9) and (10) [17, 18].

$$CHCl_3 + 3NaOR \longrightarrow HC(OR)_3 + 3NaCl \qquad (9)$$

$$3CH_3OH + HCN + HCl \longrightarrow HC(OR)_3 + NH_4Cl \qquad (10)$$

It was recognized at the onset that ketals (and to a lesser extent carbonates) are rapidly hydrolyzed under the reaction conditions employed in this study. Hydrolysis results in the formation of methanol, which can undergo reductive carbonylation to acetaldehyde. Initial experiments were carried out under anhydrous conditions with purified reagents and sublimed dicobalt octacarbonyl as the cobalt source. A typical reaction (cobalt concentration = 0.1 M, 150 ml 2,2-dimethoxypropane, temperature = 135 °C and pressure = 2250 psig) is characterized by immediate (no induction period) and rapid gas consumption that remains constant up to 40% conversion of the ketal feedstock. There was no observed difference in the reaction rate when cobalt was charged as hydrated $Co(OAc)_2 \cdot 4H_2O$. The effect of catalyst variables and operating conditions for the reaction of 2,2-dimethoxypropane with synthesis gas, eqn. (7), is given in Table 1. With a cobalt catalyst the reaction is best carried out at 135 - 140 °C and 2250 psi (H_2:CO = 1:1). Acetaldehyde rates and selectivities are typically 4.0 M h^{-1} and 60%, respectively. This rate of acetaldehyde formation is comparable to those reported for the cobalt–iodide-catalyzed reductive carbonylation of methanol (eqn. 1), which normally requires operating temperatures and pressures of 160 - 200 °C and 3000 - 6000 psig [1, 3 - 7]. Furthermore, cobalt-catalyzed (non-halide) reductive carbonylation of methanol is significantly slower. For example, we find that the initial rate of acetaldehyde formation is 0.6 M h^{-1} at 140 °C and 3000 psig with a cobalt concentration = 0.16 M and 150 ml methanol — a factor of 7 less than a comparable experiment with 2,2-dimethoxypropane (see Table 1, run 2).

In the reaction of 2,2-dimethoxypropane with synthesis gas, methyl acetate and methyl isobutyl ketone are the principal byproducts. Methyl isobutyl ketone arises from the condensation of acetone followed by hydrogenation:

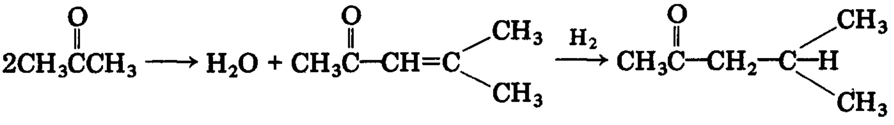
 (11)

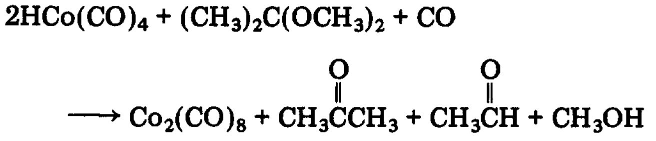
TABLE 1

Variation in catalyst composition for the reaction of 2,2-dimethoxypropane with synthesis gas[a]

Run No.	Concentration, M				Acetaldehyde	
	CoI_2	$Co(OAc)_2 \cdot 4H_2O$	ER_3	X^-	Rate ($M\ h^{-1}$)	Sel (%)
1		0.08			0.8	62
2		0.16			4.7	61
3		0.32			5.3	40
4	0.08	0.08			6.9	70
5	0.16				5.5	60
6		0.16		LiI (0.16)	8.9	65
7		0.16		LiI (0.32)	5.6	53
8		0.16		LiI (0.64)	2.5	51
9		0.16		KI (0.16)	3.1	47
10		0.16		NaI (0.16)	4.5	61
11		0.16		$CaI_2 \cdot 4H_2O$ (0.16)	4.8	50
12		0.08	PPh_3 (0.08)	LiI (0.08)	1.3	34
13	0.08	0.08	NBu_3 (0.08)		8.6	70
14	0.08	0.08	NBu_3 (0.16)		10.1	70
15	0.08	0.08	NBu_3 (0.32)		0.1	39

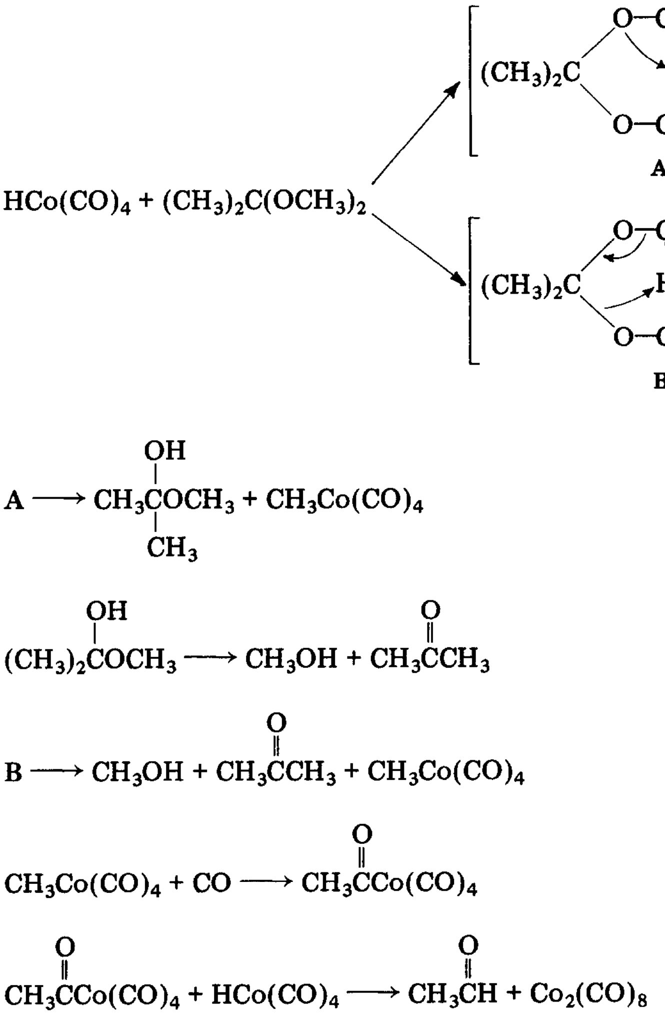
[a] All runs carried at 135 °C and 2500 psig (H_2:CO = 1:1) and 150 ml 2,2-dimethoxypropane.

High-pressure IR studies carried out at 135 °C and 2500 psi (H_2:CO = 1:1) indicate that $HCo(CO)_4$ ($\nu(CO) = 2051$, 2032 cm^{-1}) is the carbonyl species present during catalysis. It is well known that cobalt salts such as $Co(OAc)_2 \cdot 4H_2O$ are converted into $HCo(CO)_4$ under high pressures of H_2 and CO [19]. Additionally, we find that the reaction of $HCo(CO)_4$ and $(CH_3)_2C(OCH_3)_2$ carried out at 25 °C and 1 atm CO proceeds smoothly according to eqn. (12).



$$2HCo(CO)_4 + (CH_3)_2C(OCH_3)_2 + CO \longrightarrow Co_2(CO)_8 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}H + CH_3OH \tag{12}$$

The kinetics of this non-catalytic reaction were not studied in detail. However, the results are consistent with those observed in the HPIR studies, and support the intermediacy of $HCo(CO)_4$ as the catalyst/catalyst precursor in the reaction of 2,2-dimethoxypropane with synthesis gas. The reaction may proceed by the bimolecular reaction of $HCo(CO)_4$ with 2,2-dimethoxypropane, Scheme 1.



(13)

$$\mathrm{A} \longrightarrow \mathrm{CH_3\overset{OH}{\underset{CH_3}{C}}OCH_3} + \mathrm{CH_3Co(CO)_4} \quad (14)$$

$$\mathrm{(CH_3)_2\overset{OH}{C}OCH_3} \longrightarrow \mathrm{CH_3OH} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3} \quad (15)$$

$$\mathrm{B} \longrightarrow \mathrm{CH_3OH} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3} + \mathrm{CH_3Co(CO)_4} \quad (16)$$

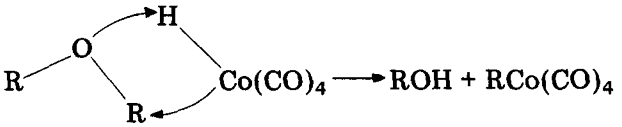
$$\mathrm{CH_3Co(CO)_4} + \mathrm{CO} \longrightarrow \mathrm{CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4} \quad (17)$$

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4} + \mathrm{HCo(CO)_4} \longrightarrow \mathrm{CH_3\overset{O}{\overset{\|}{C}}H} + \mathrm{Co_2(CO)_8} \quad (18)$$

Scheme 1.

Acetaldehyde is obtained from $CH_3Co(CO)_4$ by further reaction with CO and $HCo(CO)_4$. $CH_3Co(CO)_4$ and $CH_3C(O)Co(CO)_4$ were not observed in reaction (12) or in the catalytic reaction carried out at 135 °C and 2500 psi. It is known that steps (17) and (18) occur rapidly [20]. In the catalytic reaction, $Co_2(CO)_8$, eqn. (18), rapidly reacts with H_2 to regenerate $HCo(CO)_4$ [21].

Scheme 1 involves a four- or six-membered transition state, complexes A and B, respectively. The hemiketal obtained from A decomposes into acetone and methanol, eqn. (15) [22]. The hemiketal was not detected in the liquid products. If the reaction proceeds via the intermediacy of A, a similar reaction would be expected for alkyl ethers.



(19)

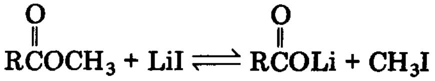
We find that dimethyl ether (1,4-dioxane solvent) or t-butyl ether fails to generate acetaldehyde with a cobalt catalyst at 135 °C and 2500 psi. Increasing the temperature and pressure to 170 °C and 5000 psi has no effect. Though not conclusive, these results imply that if the reaction of $HCo(CO)_4$ and 2,2-dimethoxypropane proceeds via Scheme 1, it does so through a six-membered transition state.

Halide-containing catalysts

In synthesis gas reactions involving a cobalt catalyst and a feedstock containing a methoxy group, addition of an iodide-containing compound markedly enhances productivity. Illustrative examples include methanol carbonylation [23 - 25], reductive carbonylation [1, 3 - 7] and homologation [26] and methyl acetate carbonylation [27]. In the reaction of 2,2-dimethoxypropane, addition of iodides typically enhances the acetaldehyde rate with valuable effects on selectivity (Table 1). The best rates, 7 - 9 M h^{-1}, are obtained with I:Co = 1:1, entries 4 and 6. Increasing the I:Co ratio by adjusting either the $CoI_2{:}Co(OAc)_2{\cdot}4H_2O$ or $LiI{:}Co(OAc)_2{\cdot}4H_2O$ ratio decreased the rate. For example, at I:Co = 4:1, entry 8, the rate is only 2.5 M h^{-1}. KI, NaI and $CaI_2{\cdot}4H_2O$ (entries 9 - 11) are slightly less effective than LiI. The rate varies in the order $Li^+ > Ca^{+2} > Na^+ > K^+$.

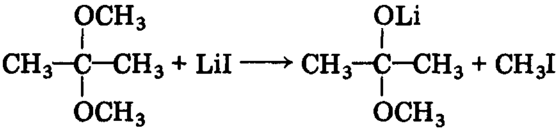
Addition of PPh_3 markedly lowers the rate (entry 12), whereas amines, especially NBu_3, promote the reaction. With I:Co = 1:1 and NBu_3:Co = 1:1 (entry 14) at 135 °C and 2500 psi, the acetaldehyde rate and selectivity are 10.1 M h^{-1} and 70%, respectively (compare with entry 4). At constant I:Co ratio (1:1) the rate increases, then decreases with increasing NBu_3:Co ratio; for example at NBu_3:Co = 4:1 there is no reaction. High-pressure IR studies carried out at 135 °C and 2500 psi (H_2:CO = 1:1) with a $CoI_2{-}Co(OAc)_2{\cdot}4H_2O{-}NBu_3$ catalyst (Co:I:NBu_3 = 1:1:1) indicate that $HCo(CO)_4$ ($\nu(CO)$ = 2051, 2031 cm^{-1}) and $Co(CO)_4^-$ ($\nu(CO)$ = 1890 cm^{-1}) [28] (approximate molar ratio of 1:1) are the principal carbonyl species present during catalysis.

It is generally accepted that iodides enhance the rate, due to the formation of CH_3I which further reacts with cobalt species present under catalytic conditions. We find that LiI (0.08 mmol) and 2,2-dimethoxypropane (0.08 mmol) react (120 °C, 2.0 h, N_2 atm) to form CH_3I in 10% yield based on charged 2,2-dimethoxypropane. The stoichiometry of the reaction was not determined. However, by analogy with the known reaction of LiI and organic esters (eqn. 20) [29],



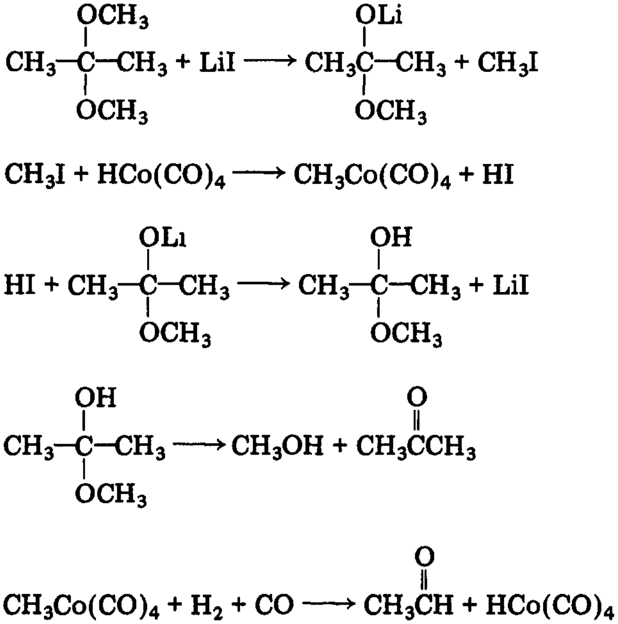
$$R\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 + LiI \rightleftharpoons R\overset{\overset{\displaystyle O}{\|}}{C}OLi + CH_3I \qquad (20)$$

it may proceed as follows:



$$\mathrm{CH_3-\underset{OCH_3}{\overset{OCH_3}{C}}-CH_3 + LiI \longrightarrow CH_3-\underset{OCH_3}{\overset{OLi}{C}}-CH_3 + CH_3I} \qquad (21)$$

Scheme 2 accounts for the observed products in the Co—LiI-catalyzed reaction of 2,2-dimethoxypropane with synthesis gas.



$$\mathrm{CH_3-\underset{OCH_3}{\overset{OCH_3}{C}}-CH_3 + LiI \longrightarrow CH_3\underset{OCH_3}{\overset{OLi}{C}}-CH_3 + CH_3I} \qquad (22)$$

$$\mathrm{CH_3I + HCo(CO)_4 \longrightarrow CH_3Co(CO)_4 + HI} \qquad (23)$$

$$\mathrm{HI + CH_3-\underset{OCH_3}{\overset{OLi}{C}}-CH_3 \longrightarrow CH_3-\underset{OCH_3}{\overset{OH}{C}}-CH_3 + LiI} \qquad (24)$$

$$\mathrm{CH_3-\underset{OCH_3}{\overset{OH}{C}}-CH_3 \longrightarrow CH_3OH + CH_3\overset{\overset{O}{\|}}{C}CH_3} \qquad (25)$$

$$\mathrm{CH_3Co(CO)_4 + H_2 + CO \longrightarrow CH_3\overset{\overset{O}{\|}}{C}H + HCo(CO)_4} \qquad (26)$$

Scheme 2.

Scheme 2 is somewhat simplified, in that the reactions described by eqns. (23) and (26) are more complex than shown [30 - 32]. Only trace amounts of CH_3I were found in the product mixture, raising the possibility that iodide serves mainly to increase the $Co(CO)_4^-$ concentration via formation of species such as $[Co(I)_x(CO)_y][Co(CO)_4]$ or $Li[Co(CO)_4]$ [33, 34].

The stoichiometry of eqn. (7) requires the consumption of one mole H_2 per mole CO. As shown in Table 2, increasing the H_2:CO feed ratio to 2:1 has little impact on acetaldehyde rate and selectivity (compare entry 2, Table 2 with entry 14, Table 1). At H_2:CO = 1:2, the acetaldehyde selectivity is significantly reduced. In this case the principal product is methyl acetate. Increasing the pressure (H_2:CO = 1:1) at constant temperature (150 °C, entries 3 - 5) increases both rate and selectivity. Increasing the temperature to 180 °C at 2500 psi increases rate, however a significant loss in acetaldehyde results due to the formation of large amounts of methyl acetate and heavy unknowns.

TABLE 2

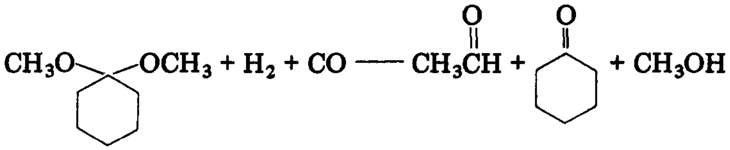
Variation in reaction conditions for the reaction of 2,2-dimethoxypropane with synthesis gas[a]

Run No.	Temp. (°C)	Pressure (psig)	H_2 CO	Rate ($M\ h^{-1}$)	Selectivity (%)
1	135	2500	1:2	1.2	36
2	135	2500	2:1	6.8	60
3	150	1000	1:1	0.3	25
4	150	1500	1.1	3.1	50
5	150	2000	1:1	7.0	60
6	180	2500	1:1	11.5	35

[a] All runs carried out with $[CoI_2] = 0.08$ M, $[Co(OAc)_2 \cdot 4H_2O] = 0.08$ M, $[NBu_3] = 0.08$ M and 150 ml of 2,2-dimethoxypropane.

CoI_2 and Co—I—NBu_3 are known catalysts for the reaction of methanol with synthesis gas to produce acetaldehyde, eqn. (1) [1, 3 - 7, 35]. Temperatures of 160 °C and pressures of 2500 psi are normally required. We find that the initial rate of acetaldehyde formation via reductive carbonylation of methanol is only 0.65 M h^{-1} at 135 °C and 2500 psi with a Co—I—NBu_3 catalyst. Thus, to a small extent this reaction occurs in conjunction with the reaction of 2,2-dimethoxypropane with synthesis gas.

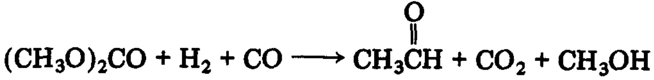
1,1-Dimethoxycyclohexane and dimethoxydiphenylmethane were examined as substrates at similar reaction conditions employed with 2,2-dimethoxypropane. The reaction of 1,1-dimethoxycyclohexane with synthesis gas results in the formation of acetaldehyde, methanol and cyclohexanone according to eqn. (27).



(27)

At 135 °C and 2500 psi (H_2:CO = 1:1) with Co:I:NBu_3 = 1:1:1, the acetaldehyde rate and selectivity are 2.7 M h^{-1} and 72%, respectively. The reactivity of dimethoxydiphenylmethane was markedly less, with the best rate, 0.1 M h^{-1}, occurring with a Co—I catalyst at 135 °C and 2500 psi.

Dimethyl carbonate reacts with synthesis gas in the presence of a cobalt–LiI catalyst, resulting in the formation of acetaldehyde, CO_2 and CH_3OH:



$$(CH_3O)_2CO + H_2 + CO \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}H + CO_2 + CH_3OH \qquad (28)$$

Other products include trace amounts of methane, ethanol and methyl acetate. An iodide promoter is required. Cobalt alone will not catalyze the reaction over the range 135 to 180 °C and 2500 to 5000 psig. With a catalyst charge consisting of $Co(OAc)_2 \cdot 4H_2O$ and CoI_2 (total [Co] = 0.160 M) and [LiI] = 0.160 M, at 135 °C and 2500 psi the acetaldehyde rate and selectivity are 1.4 M h^{-1} and 82%, respectively, Table 3. Increasing the pressure to 4000 psi (Table 3, entry 2) increased the rate to 3.4 M h^{-1} with little change in selectivity. Increasing the temperature to 180 °C and 4000 psig markedly increased the rate, to 28.5 M h^{-1}. In this case the selectivity was 87%. At temperatures above 180 °C the activity decreases. For example, the acetaldehyde rate and selectivity are only 0.2 M h^{-1} and 16%, respectively, at 200 °C and 4000 psig. The loss in activity at higher temperatures is accompanied by precipitation of a large amount of unidentified cobalt-containing solids. A significant rate decrease is also observed if the LiI concentration is increased from 0.160 M to 0.320 M (Table 3, entries 5 and 6). Replacing LiI with $CaI_2 \cdot 4H_2O$ (0.160 M) or KI (0.160 M) lowers the acetaldehyde rate to 12.1 M h^{-1} and 1.0 M h^{-1}, respectively, at 180 °C and 4000 psi.

In general, addition of amines or phosphines reduces the rate. For example, with [Co] = 0.160 M, [LiI] = 0.160 M and NBu_3 = 0.080 M at 180 °C and 4000 psi, the acetaldehyde rate is 12.2 M h^{-1} compared to 28.5 M h^{-1} without added NBu_3. Significantly lower rates are obtained with PPh_3, Table 3.

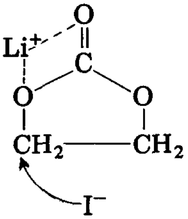
We find that methyl iodide is obtained from the reaction of dimethyl carbonate with LiI. For example, heating dimethyl carbonate (300 mmol) and LiI (30 mmol) to 150 °C under N_2 for 3 h results in the formation of CH_3I, CH_3OCH_3 and CO_2. A similar reaction is known for the reaction of ethylene carbonate with LiI [36].

TABLE 3

Variation in operating conditions for the reaction of dimethyl carbonate with synthesis gas[a]

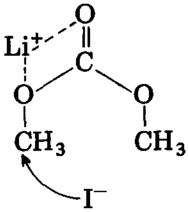
Entry No.	Concentration, M				Temp (°C)	Pressure (psig)	Acetaldehyde	
	$[CoI_2]$	$[Co(OAc)_2 \cdot 4H_2O]$	[LiI]	$[ER_3]$			Rate (M h^{-1})	Sel. (%)
1	0.080	0.080	0.160	—	135	2500	1.4	82
2	0.080	0.080	0.160	—	135	4000	3.4	79
3	0.080	0.080	0.160	—	180	4000	28.5	87
4	0.080	0.080	0.160	—	200	4000	0 2	16
5	0.080	0.080	0.240	—	180	4000	0.2	28
6	0.080	0.080	0.320	—	180	4000	0.1	18
7	0.080	0.080	0.160	NBu_3	180	4000	12.2	85
8	0.080	0.080	0.160	PPh_3 (0.080)	180	4000	0.2	17
9	0.80	0.080	0.160	—	180	3500	6.6	70

[a] All runs carried out with 150 ml dimethyl carbonate (solvent-free) except entry 9, which utilized 75 ml dimethyl carbonate and 75 ml methanol.



$\longrightarrow ICH_2CH_2OCO_2Li \longrightarrow ICH_2CH_2OLi + CO_2$ (29)

In the case of dimethyl carbonate, the reaction may proceed as follows:



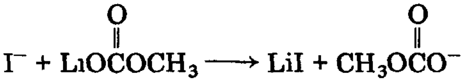
$\longrightarrow CH_3I + CH_3OCO_2Li$ (30)

$CH_3OCO_2Li \longrightarrow LiOCH_3 + CO_2$ (31)

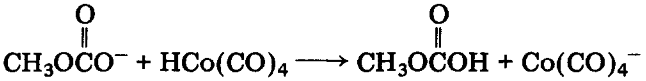
$LiOCH_3 + CH_3I \longrightarrow LiI + CH_3OCH_3$ (32)

Taking into account the fact that LiI cleaves dimethyl carbonate, a plausible mechanism for the formation of acetaldehyde is outlined in eqns. (33) - (36):

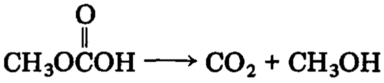
$CH_3I + Co(CO)_4^- \longrightarrow CH_3Co(CO)_4 + I^-$ (33)



$$I^- + LiO\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow LiI + CH_3O\overset{\overset{O}{\|}}{C}O^-$$ (34)



$$CH_3O\overset{\overset{O}{\|}}{C}O^- + HCo(CO)_4 \longrightarrow CH_3O\overset{\overset{O}{\|}}{C}OH + Co(CO)_4^-$$ (35)



$$CH_3O\overset{\overset{O}{\|}}{C}OH \longrightarrow CO_2 + CH_3OH$$ (36)

Acetaldehyde is obtained from $CH_3Co(CO)_4$ as indicated in Scheme 1. LiI is regenerated via eqn. (34). Dimethyl ether is a minor product in the catalytic reaction, indicating that step 32 is insignificant in the presence of the cobalt catalyst. The acetaldehyde rate increase as a function of metal cation, *i.e.* $Li^+ > Ca^{++} > K^+$, is consistent with the notion of cation-assisted cleavage of dimethyl carbonate (eqn. 30). The harder acids (cations, *i.e.*, Li^+) would be expected to be more effective in assisting cleavage of dimethyl carbonate since they should form stronger complexes with dimethyl carbonate [37].

As in the case of methyl ketals, the methanol co-product can undergo reductive carbonylation, eqn. (1), especially at the higher operating conditions of 180 °C and 4000 psi. Water produced via eqn. (1) can hydrolyze dimethyl carbonate:

$$(CH_3O)_2CO + H_2O \longrightarrow 2CH_3OH + CO_2 \tag{37}$$

Addition of eqns. (1) and (37) yields eqn. (29). However, for the following reasons we conclude that the reductive carbonylation of methanol is a minor process in the reaction of dimethyl carbonate and synthesis gas. At 180 °C and 4000 psi with $CoI = 0.080$ M, $Co(OAc)\cdot 4H_2O = 0.080$ M, $LiI = 0.160$ M and 150 ml methanol, the initial rate of acetaldehyde formation is 5.0 M h^{-1}. Adding CO_2 has little, if any, effect on the reaction. Diluting the methanol with an inert solvent further decreases the rate of acetaldehyde formation [1]. In the data reported in Table 3, the dimethyl carbonate conversion was maintained at 40%. In this case the build-up of methanol is limited, *i.e.* the methanol concentration is low, and the observed rate far exceeds that expected if dimethyl carbonate had simply functioned as a diluent. In related experiments, the addition of methanol to dimethyl carbonate (constant total volume) decreased the rate from that normally observed for neat dimethyl carbonate. For example, with a 50:50 vol.% mixture of dimethyl carbonate and methanol the rate is decreased by a factor of 4 (compare entries 3 and 9, Table 3). These results suggest that methanol serves mainly as a diluent and not a substrate in the reaction of dimethyl carbonate with synthesis gas.

Conclusion

Dimethyl carbonate and 2,2-dimethoxypropane react readily with synthesis gas in the presence of a cobalt or cobalt–iodide-based catalyst to produce acetaldehyde. These reactions are facilitated by the formation of a C=O bond in the byproduct, acetone in the 2,2-dimethoxypropane reaction and CO_2 in the dimethyl carbonate reaction. Neither reaction directly produces H_2O; however, the requirement to recycle the byproducts and reform the ketal or carbonate is an additional step. But, in both cases this disadvantage is partially offset by either reduced pressure or higher rates. Ketal hydroformylation proceeds at good rates (5 - 10 M h^{-1}) to acetaldehyde at relatively low temperature and pressure (135 °C, 2250 psi). The reaction can be carried out with a cobalt catalyst (halide-free), but addition of an iodide-containing compound and NBu_3 (Co—I—NBu_3) markedly enhances the rate. The reaction of dimethyl carbonate with synthesis gas is a relatively high pressure (4000 psig) process, but the rates are significantly higher than in the reductive carbonylation of methanol (~30 *vs.* 12 M h^{-1}). The best catalyst consists of $Co(OAc)_2\cdot 4H_2O$:CoI_2:LiI at a molar ratio of 1:1:2.

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