THE ROLE OF PHOSPHINES AND SOLVENTS IN CoI₂-CATALYZED REDUCTIVE CARBONYLATION OF METHANOL

RICHARD W. WEGMAN and DAVID C. BUSBY

Union Carbide Corporation, P. O. Box 8361, South Charleston, WV 25303 (U.S.A.) (Received September 18, 1984; accepted January 9, 1985)

Summary

The role of triphenylphosphine and solvents in the CoI_2 -catalyzed reductive carbonylation of methanol to acetaldehyde has been studied. When utilized within a controlled molar range, triphenylphosphine has little, if any, effect on the acetaldehyde rate and selectivity. It does serve to reduce corrosion to an acceptable level. Acetaldehyde selectivity is markedly improved by use of a solvent. With few exceptions, most solvents readily decompose under reaction conditions.

Introduction

It is well known that methanol, which is first made from synthesis gas, can be further reacted with synthesis gas by reductive carbonylation, homologation, or carbonylation to make acetaldehyde, ethanol and acetic acid, respectively [1]. Unsatisfactory conversion and selectivity have prevented commercialization of the reductive carbonylation or homologation technology. Additionally, fermentation routes to ethanol have now become economically competitive with synthesis gas-based processes [2, 3]. Reductive carbonylation of methanol has received some attention in the literature [4 - 9]. Acetaldehyde can be used as a building block for numerous chemicals, for instance (i) condensation to higher aldehydes and alcohols, (ii) esters via the Tishenko reaction, specifically formation of ethyl acetate which can be readily cracked to acetic acid and ethylene, and (iii) vinyl ethers from various acetal derivatives.

The reductive carbonylation of methanol is catalyzed, at least to some extent, by most Group VIII transition metals used in conjunction with a halogen promoter [10]. Of the Group VIII metals, cobalt has received the most attention. Halogen compounds (covalent or ionic) containing Cl, Br, or I promote the reaction, but iodides give the best reaction rates [11]. In addition to metal and halide components, additional promoters of the form ER_3 (E = N, P, As, Sb, Bi; R = organic moiety) are frequently used. Triaryl phosphines have been reported to enhance the ethanol selectivity at the

expense of acetaldehyde whereas triaryl arsines and stibines increase the acetaldehyde selectivity at the expense of ethanol [7].

Here we wish to report the selective formation of acetaldehyde via a cobalt-iodide-phosphine catalyst. High conversion, rate and selectivity can be obtained with the proper selection of solvent, catalyst concentration, temperature and pressure. Also, solvent decomposition and corrosivity will be addressed.

Experimental

All chemicals were reagent grade and were used without further purification. Triphenylphosphine, iodine, methyl iodide and methanol were obtained from MCB. $Co(OAc)_2 \cdot 4H_2O$ was purchased from Mallinckrodt, anhydrous cobaltous iodide from Research Organic-Inorganic and triphenylphosphine oxide from Alfa.

The high pressure experiments were carried out in a 300 ml Hastelloy C autoclave. In a typical experiment $Co(OAc)_2 \cdot 4H_2O$ (8.0 mmol), I_2 (14.0 mmol) and PPh₃ (30.8 mmol) or 8.0 mmol of preformed complexes are charged under N₂ to a clean reactor containing 150 ml CH₃OH. The reactor is sealed, purged with synthesis gas and pressured to 2000 psig with synthesis gas. Agitation (750 rpm) is begun and the reactor heated to the desired temperature within 40 min. At reaction temperature the reactor is pressured to 5250 psig. The reaction is allowed to consume gas until the pressure has fallen to 4750 psig. The reactor is repressured to 5250 psig and cycled in this manner for 10000 psig total uptake. The reactor contents are then cooled via internal cooling coils to 10 °C. A vapor phase sample is taken for analysis, and the liquid contents are placed in a chilled bottle. Gaseous products were analyzed on a Carle III-H chromatograph. Liquid products were analyzed with a Hewlett-Packard Model 5880 gas chromatograph equipped with two 1/8 in \times 10 ft 60/70 mesh Chromasorb 101 columns connected in series.

The acetaldehyde rates are expressed as Mhr^{-1} (mol l^{-1} h^{-1}) and are based on liquid volume. The acetaldehyde selectivity is calculated via

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

where AcH equals acetaldehyde and DMA is 1,1-dimethoxyethane. The methanol conversion is calculated via

Methanol conversion

$$= \frac{(\text{moles MeOH fed}) - (\text{moles MeOH found}) + (2 \times \text{moles DMA})}{\text{moles MeOH fed}} \times 100\%$$

In the methanol conversion formula, moles of methanol found does not include methanol equivalents in methyl acetate and dimethyl ether. However, due to their ease of recovery the methanol equivalents in 1,1dimethoxyethane are included.

The solvent screening experiments were carried out as follows. $Co(OAc)_2 \cdot 4H_2O$, I_2 and PPh₃ in a 1:2:2 molar ratio were charged to the reactor containing CH₃OH and the solvent. The CH₃OH:solvent ratio = 0.33:1 (by volume, total volume = 150 ml). The reaction was carried out at 170 °C and 5000 psig for a total gas consumption of 3000 psi. The products were analyzed as described above.

Preparation of $CoI_2(OPPh_3)_2$

 $CoI_2(anhydrous)$ (40.0 g, 127.9 mmol) was dissolved in 500 ml of argon-degassed acetone. The green solution was filtered to remove a small amount of gray powder. OPPh₃ (73.0 g, 262.3 mmol) was dissolved in 400 ml argon-degassed acetone, and the CoI_2 solution was added to it. The mixture was magnetically stirred under argon for 1 h, and the resulting airstable blue crystalline material was filtered off, washed with two portions of hexane and two portions of acetone and dried on the frit. Yield 101.5 g, 91.4%. The complex was characterized by comparison of its IR spectrum with published data (ν (P=O) 1150 cm⁻¹) [12].

Preparation of $[MePPh_3]_2[CoI_4] \cdot (CH_3)_2CO$

The complex was prepared by an extension of the method of Nyholm and Gill [13]. [MePPh₃]I (12.94 g, 32.0 mmol) was dissolved in 350 ml of argon-degassed acetone. CoI_2 (5.00 g, 167.0 mmol) was dissolved in 100 ml of acetone and the green solution filtered to remove some gray solid. The CoI_2 solution was added to the [MePPh₃]I solution and the mixture stirred under argon for 3 h. The resulting air-stable green crystalline material which formed was filtered off, washed with a small amount of acetone and dried on the frit to give 11.2 g product. The filtrate was concentrated *in vacuo* to about 1/4 its original volume, and an additional 5.5 g of product was obtained. Addition of hexane to the filtrate produced another 1.3 g of product. Total yield 18.0 g, 95.5%. This material was characterized by IR and NMR spectroscopy and was identical to the green material isolated from a catalytic run which is described below, except for differing solvent of crystallization.

Isolation of complexes from a catalytic run

The catalytic solution from a typical run $(Co(OAc)_2 \cdot 4H_2O, 8.0 \text{ mmol}; I_2, 14.0 \text{ mmol}; PPh_3, 30.8 \text{ mmol}; 170 °C, 5000 \text{ psig}, 2.0 h, H_2:CO = 1:1) was transferred from the receiver bottle in which it was stored to a 500 ml round-bottomed flask. The flask was fitted with a stopcock, and the solvent was removed$ *in vacuo* $<math>(10^{-4} \text{ torr}, 35 °C)$ to give a green oil. A small amount of acetone was added to the oil, which converted to a green powder on scratching. The powder was filtered off and washed thoroughly with CH₂Cl₂ which removed some blue material. The remaining green material was recrystallized from acetone/hexane. An analytical sample of this material was recrystallized from CH₂Cl₂/heptane. Analysis Calcd. for C₃₉H₃₈Cl₂COI₄P₂

 $([MePPh_3]_2[CoI_4] \cdot CH_2Cl_2)$: C, 38.84; H, 3.18; Co, 4.89; I, 42.90; P, 5.14. Found: C, 39.09; H, 3.41; Co, 4.69; I, 40.90; P, 5.23.

The blue CH_2Cl_2 wash from above was evaporated to dryness to give a blue powder which was shown by IR spectroscopy to be fairly pure $CoI_2(OPPh_3)_2$.

A description of the high-pressure IR equipment, including the highpressure infrared cell and spectrometer together with the usual operation procedure, has already appeared [14]. ³¹P NMR spectra were obtained on a Varian FT-80A spectrometer at 32.2 MHz and are referenced to external H_3PO_4 .

Results and discussion

Initial experiments were carried out with a halide-free cobalt catalyst [15]. In methanol (no solvent) with a cobalt concentration of 0.08 M, (total cobalt charged) acetaldehyde rates and selectivities are typically 1.0 Mhr⁻¹ and 60% at 170 °C and 5000 psi (H₂:CO = 1:1). Ethanol (5 - 10%), methyl acetate (10 - 20%), dimethyl ether (1 - 5%) and methane (0 - 2%) are the major byproducts. It is generally thought that ethanol is obtained from the reduction of acetaldehyde [16]. Consistent with previous reports, increasing the temperature or H₂:CO ratio increased ethanol selectivity [15].

 $HCo(CO)_4$ ($\nu(CO)$ 2050, 2030 cm⁻¹) [17] and $Co(CO)_4^-$ ($\nu(CO)$ 1890 cm⁻¹) [18] (1:10 ratio) were identified by their characteristic CO stretching frequencies via high-pressure IR experiments carried out during the reaction at 170 °C and 5000 psi. There was no indication of $Co_2(CO)_8$ as judged by the lack of bridging CO bands in the IR spectra [17]. The importance of $Co(CO)_4^-$ in the iodide-promoted system has been previously reported [7]. Addition of PPh₃ over the range PPh₃:Co = 0.5:1 to 2:1 resulted in a marked decrease in catalytic activity. $HCo(CO)_3PPh_3$, identified via high-pressure IR, is the major species present under reaction conditions.

As described in the introduction, iodide promoters dramatically increase the activity of cobalt catalysts. Several studies have been published that describe the effect of temperature and pressure on the iodide-promoted reaction [4-9]. We have found it particularly advantageous to operate at 170 °C and 5000 psi (1:1). Several iodide-containing complexes were examined as catalysts, and the results are summarized in Table 1. Besides increasing the rate, these complexes increase the acetaldehyde selectivity by 10 to 15% over that normally observed with a halide-free cobalt catalyst. The ethanol selectivity drops, indicating that added iodide decreases the reducing ability of the cobalt catalyst.

Addition of CoI_2 dissolved in methanol results in an immediate color change from dark brown to pink, which is characteristic of Co(II) solvated by methanol. This mixture at 170 °C and 5000 psi converts MeOH to acetaldehyde at rates and selectivities of 7.0 Mhr⁻¹ and 78%. $\text{CoI}_2(\text{PPh}_3)_2$ also undergoes a similar color change when dissolved in methanol, and the ³¹P NMR spectrum of such a solution displays a somewhat broadened peak

Catalyst charge	AcH		EtOH		MeOAc	
	Rate	Sel	Rate	Sel	Rate	Sel
Cal ²	7.0	78	0.1	2.0	1.3	16.4
$CoI_2(PPh_3)_2$	6.9	77	0.3	2.7	1.1	15.2
$CoI_2(PPh_3)_2 + PPh_3$	4.9	72	0.3	3.9	0.74	18.2
$CoI_2(PPh_3)_2 + 2PPh_3$	0.3	90	0.01	1.2	0.02	3.7
$CoI_2(PPh_3)_2 + 2PPh_3 + 2CH_3I$	7.5	72	0.2	1.9	1.4	20.6
$CoI_2(OPPh_3)_2$	7.2	77	0.2	1.4	1.2	15.5
$CoI_2(OPPh_3)_2 + 2OPPh_3$	6.0	76	0.2	2.2	1.0	17.4
$CoI_2(OPPh_3)_2 + 2PPh_3$	6.5	77	0.3	3.4	1.1	15.3
$CoI_2(OPPh_3)_2 + 4PPh_3$	0.3	89	0.02	1.4	0.02	2.8

 TABLE 1

 Cobalt-based catalysts for the reductive carbonylation of methanol^a

^a All runs = 170 °C, 5000 psi with [Co] = 0.052 M. Methanol conversion maintained at 50%. Rates are reported as MHr^{-1} and selectivities as percent.

centered at -5.8 ppm and assigned to free PPh₃. The peak broadening is presumably due to PPh₃ exchanging with Co(II). At 10 °C and 1 atm CO we find that CoI₂(PPh₃)₂ (in methanol) is readily converted to CoI(CO)₂(PPh₃)₂ [19]. The reduction of Co(II) is thought to proceed according to eqn. (1) [20].

$$5\text{CoI}_2(\text{PR}_3)_2 + 8\text{CO} \longrightarrow 4\text{CoI}(\text{CO})_2(\text{PR}_3)_2 + \text{CoI}_2 + 2\text{PR}_3\text{I}_2 \tag{1}$$

Heating the mixture to 170 °C and pressuring to 5000 psi (H_2 :CO = 1:1) results in loss of $CoI(CO)_2(PPh_3)_2$. An IR spectrum of the reaction mixture displays an intense band at 1890 cm⁻¹ due to $Co(CO)_4$, two weak bands at 2030 and 2050 cm^{-1} and a medium band at 1975 cm^{-1} . The bands at 2030 and 2050 $\rm cm^{-1}$ have been previously reported in a non-phosphine-containing cobalt-iodide catalyst, and are thought to be due to $[Co(CH_3OH)_x(CO)_vI]^{n+1}$ [7]. The band at 1975 cm^{-1} is possibly due to HCo(CO)₃PPh₃, which is observed with a cobalt-PPh₃ catalyst. $[Co(CO)_3(PPh_3)_2]I$, which is known to form in the reaction of $CoI_2(PPh_3)_2$ and CO at 2500 psi and 80 °C, is not observed [21]. When $CoI_2(PPh_3)_2$ was used as a catalyst, the acetaldehyde rate and selectivity were very similar to those for CoI_2 alone (Table 1). A ³¹P NMR spectrum of the recovered catalyst solution showed a single sharp peak at 21 ppm assigned to $[CH_3PPh_3]^+$; there was no observable signal for PPh₃. An IR spectrum did not show CO stretches assignable to a cobalt carbonyl species. The cobalt was recovered as a mixture of $[CoI_{4-n}(OAc)_n]^{2-}$ (vida infra). Cobalt anions of the form $[CoI_{4-n}(OAc)_n]^{2-1}$ have been previously reported to be the predominant species under reaction conditions (species identified by UV-visible spectroscopy) in both carbonylation and hydroformylation of methanol using a $Co(OAc)_2 \cdot 4H_2O/I^-$ catalyst [22, 23].

A mixture of $CoI_2(PPh_3)_2$ and one or two equiv of PPh_3 resulted in low catalytic activity; however, activity is regained via addition of CH_3I such that

the CH₃I:PPh₃ molar ratio is 1:1. A 0.052 M solution of $CoI_2(OPPh_3)_2$ gave acetaldehyde rates and selectivities similar to CoI_2 or $CoI_2(PPh_3)_2$. A ³¹P NMR spectrum of the recovered catalyst solution showed a single broad peak centered at 35 ppm assigned to OPPh₃. $CoI_2(OPPh_3)_2$ was recovered from the reaction mixture in 80% yield. Addition of 2 equiv of OPPh₃ or PPh₃ to a solution of $CoI_2(OPPh_3)_2$ had negligible effect on catalytic activity, whereas 4 equiv of PPh₃ resulted in a marked decrease.

The results indicate that $OPPh_3$ has little, if any, impact on the activity of a CoI_2 catalyst. This is also true for PPh_3 when it is used within a welldefined range. The critical variable is the PPh_3 :I ratio, where I represents total iodide charged including the iodide equiv contained in CoI_2 . If the PPh_3 :I ratio exceeds 1:1 (Table 1) then substantial loss in catalytic activity is observed. As described later, the reaction is normally carried out with added PPh₃ in order to prevent corrosion.

Charging the catalyst as a mixture of a cobalt salt (such as $Co(OAc)_2 \cdot 4H_2O$), I_2 , PPh₃ and CH₃OH can lead to false conclusions regarding catalytic activities and dependencies, because unrecognized reactions may be occurring prior to the attainment of the desired operating conditions. For example, in the absence of $Co(OAc)_2 \cdot 4H_2O$, we find that I_2 and PPh₃ rapidly react with the CH₃OH solvent at 25 °C to form CH₃I, OPPh₃ and H₂O.

$$I_2 + PPh_3 \longrightarrow I_2PPh_3 \tag{2}$$

$$I_2PPh_3 + CH_3OH \longrightarrow OPPh_3 + CH_3I + HI$$
(3)

(4)

))

$$HI + CH_3OH \longrightarrow CH_3I + H_2O$$

In the presence of excess PPh₃, CH₃I reacts to form the phosphonium salt [CH₃PPh₃]I. Product formation is complete within 10 min as judged by ³¹P NMR. The reaction of alcohols with P(V) species of the form R₃PX₂ (R = aryl, alkyl; X = Cl, Br, I) is known and has been exploited for the preparation of organic halides [24, 25].

At 25 °C a 1:2:2 molar ratio of $Co(OAc)_2 \cdot 4H_2O$, I_2 and PPh₃ dissolved in methanol generates $CoI_2(OPPh_3)_2$ via eqns. (2), (3), (5) and (6) in 80% yield. HI, obtained via eqn. (3), initially reacts with $Co(OAc)_2 \cdot 4H_2O$ to generate CoI_2 as shown in eqn. (5). With excess PPh₃ ($1 < PPh_3:I_2 < 2$), a mixture of $CoI_2(OPPh_3)_2$ and $[CH_3PPh_3]_2[CoI_4]$ is obtained, eqns. (6) and (7). At PPh₃:I₂ ratios greater than 2:1, $[CH_3PPh_3]_2[CoI_4]$ is the principal product.

$$2HI + Co(OAc)_2 \longrightarrow CoI_2 + 2HOAc$$
(5)

$$\operatorname{CoI}_2 + \operatorname{OPPh}_3 \longrightarrow \operatorname{CoI}_2(\operatorname{OPPh}_3)_2$$
 (6)

$$2[CH_{3}PPh_{3}]I + CoI_{2}(OPPh_{3})_{2} \longrightarrow [CH_{3}PPh_{3}]_{2}[CoI_{4}] + 2OPPh_{3}$$
(7)

A series of experiments were carried out in order to examine the effect of added HI. In these experiments (170 $^{\circ}$ C, 5000 psig, 2.0 h, 150 ml CH₃OH)



Fig. 1. The rate of acetaldehyde formation as a function of initial $[HI]^2$ at constant $[I^-]$.

the catalyst charge consisted of $Co(OAc)_2 \cdot 4H_2O$ (4.0 mmol), PPh₃ (15.4 mmol), and varying amounts of HI and KI such that a constant I⁻ concentration (I⁻ = 15.4 mmol) was maintained. As shown in Fig. 1, at constant [I⁻] the acetaldehyde rate increases linearly with the square of the initial [HI]. This second order dependence is only observed with $Co(OAc)_2 \cdot 4H_2O$. For example, the rate remains relatively unchanged when CoI_2 is utilized with combinations of HI and KI. A rate enhancement is not observed with protonic acids other than hydrohalic acids. In all likelihood, the second order dependence is a result of the transformation of $Co(OAc)_2 \cdot 4H_2O$ into CoI_2 via eqn. (5) upon charging of the reagents. A rate enhancement over a limited range of added HI to a $Co(OAc)_2 \cdot 4H_2O$ —LiI catalyst has been noted [9].

In experiments carried out at 170 °C and 5000 psi with a catalyst charge consisting of $Co(OAc)_2 \cdot 4H_2O:I_2:PPh_3 = 1:2:2$ (molar basis, [Co] = 0.052 M) acetaldehyde rates and selectivities are 6.8 Mhr⁻¹ and 77%. These results are nearly identical to those observed with $CoI_2(OPPh_3)_2$, Table 1, which is expected based on the stoichiometry of eqns. (2) through (6). Similar results were obtained with $Co(OAc)_2 \cdot 4H_2O:I_2:PPh_3 = 1:2:4$. A ³¹P NMR spectrum of the recovered catalyst solution showed a sharp peak at 21 ppm assigned to $[CH_3PPh_3]^+$, and a broad peak centered at 35 ppm assigned to OPPh₃ exchanging with paramagnetic Co(II). From this reaction mixture, the cobalt complex $[CH_3PPh_3]_2[CoI_4]$ was isolated in 45% yield based on charged cobalt. $CoI_2(OPPh_3)_2$ was also a major product but was not quantified due to its difficulty in purification. These results demonstrate that excess PPh_3 , which is not oxidized by I_2 and CH_3OH , is quaternized by CH_3I to form $[CH_3PPh_3]I$ which further reacts with $CoI_2(OPPh_3)_2$ according to eqn. (7). Hence, with a $Co(OAc)_2 \cdot 4H_2O:I_2:PPh_3 = 1:2:4$ catalyst charge, $CoI_2(OPPh_3)_2$ and $[CH_3PPh_3]_2[CoI_4]$ account for the bulk of the catalyst components both before and after catalysis.

Solvent	Reaction time (h)	CH ₃ OH conversion	AcH		EtOH		MeOAc	
			Rate	Sel	Rate	Sel	Rate	Sel
diphenyl ether	1.15	66	1.8	88	0.07	3.4	0.05	3.5
THF	0.38	45	3.6	90	0.0	0.0	0.2	4.0
2-ethoxyethyl ether	0.48	64	5.4	86	0.2	2.5	0.2	5.9
1.4-dioxane	0.51	71	3.5	87	0.09	2.3	Trace	
n-propanol	0.45	56	1.8	73	0.2	7.1	b	
iso-propanol	0.58	53	3.9	89	0.3	6.6	0.03	3.0
ethylene glycol	1.23	45	0.2	low	0.03	7.6	0.1	3.6
1,4-butanediol	0.98	72	1.9	25	c		c	
2.5-hexanediol	0.53	65	3.8	87	0.1	4.3	0.1	3.6
methyl ethyl ketone	0.51	52	4.4	86	0.06	1.0	0.3	8.0
2.5-hexanedione	0.82	66	1.9	74	0.03	1.2	0.4	2.1
nonane	1.68	56	3.1	84	0.2	4.8	0.2	5.8
toluene	0,9	62	4.2	86	0.2	3.7	0.2	5.6

132

The effect of solvents in the reductive carbonylation of methanol^a

^aAll runs = 170 °C, 5000 psig with [Co] = 0.052 M, $[I_2] = 0.104$ M and $[PPh_3] = 0.104$ M. Rates are reported as Mhr⁻¹. Selectivities and conversions are reported as percent.

^bNot well resolved via GC.

^cComplex reaction mixture due to solvent decomposition.

Acetaldehyde selectivity is improved at the expense of reaction rate by the addition of a solvent. Numerous solvents were screened (Table 2) including ethers, polyethers, alcohols, polyols, ketones and alkanes. Only the selectivities to the three major products, acetaldehyde, ethanol and methyl acetate, are reported in Table 2. Other species accounting for the remainder of the products include dimethyl ether, methane, diethyl ether, crotonaldehyde and n-butanol. The latter two products, acetaldehyde condensation products, were formed in trace amounts. They are known to be generated in moderate yields under longer reaction times or with Co-I-(R2PS)2 or Co-I-RSR catalysts [29, 30]. In most cases the solvents examined in this study decomposed. Many species are capable of causing or aiding in solvent decomposition. Most noteworthy are I^- , CH₃I, H₂O and strong acids such as HI and possibly $HCo(CO)_4$. Solvent decomposition can occur in a variety of ways including (i) acid cleavage of ether linkages [26, 27], (ii) well known hydrolysis and halogenation reactions, (iii) participation in condensation reactions with acetaldehyde, and (iv) reaction as substrates for synthesis gas conversions such as hydrogenation, reductive carbonylation, homologation and carbonylation [28].

In general, the best acetaldehyde rates and selectivities, typically 3 to 5 Mhr^{-1} and 80 to 90%, are obtained in ethers and polyethers. These solvents have excellent solubility properties, especially for maintaining homogeneous mixtures during product refining; however, all but diphenyl ether decompose rapidly. For example, the highest acetaldehyde rate for any solvent is ob-

served with tetraglyme (6.6 Mhr⁻¹); however, tetraglyme rapidly decomposes to triethylene glycol and methoxytetraethylene glycol. Triethylene glycol is a reasonable solvent, but eventually decomposes to ethylene glycol and diethylene glycol which are extremely poor solvents. Somewhat lower rates are obtained with alcohols and polyols. There is a distinct increase in acetaldehyde rate and selectivity on going from primary to secondary alcohols, typically 1.5 - 2.0 Mhr⁻¹ and 75% in primary alcohols and 2.5 - 3.5 Mhr⁻¹ and 85% in secondary alcohols. This same trend is also observed in polyols; 1,4-butanediol gives low rate/selectivity whereas 3,5-hexanediol gives high rate/selectivity. The origin of this rate and selectivity enhancement is unclear. One plausible explanation is that secondary alcohols transfer methyl groups as shown below [28].

$$\begin{array}{c} H \\ H \\ R - C - OH + CH_{3}OH \xrightarrow{H^{+}} R - C - O - CH_{3} + H_{2}O \\ H \\ R \\ R \end{array}$$
(8)

$$\begin{array}{c} H \\ R - C - OCH_3 + Co(CO)_4^- \longrightarrow CH_3Co(CO)_4 + R - C - O^- \\ R \\ R \end{array}$$
(9)

$$\begin{array}{c} H \\ R - C - O^{-} + HCo(CO)_{4} \longrightarrow R - C - OH + Co(CO)_{4}^{-} \\ R \\ R \\ R \end{array}$$
(10)

 $\begin{array}{c} O \\ \parallel \\ CH_{3}Co(CO)_{4} + H_{2} + CO \longrightarrow CH_{3}CH + HCo(CO)_{4} \end{array}$ (11)

All of the primary and secondary alcohols tested (C_2 thru C_5) decompose during long-term operation. The major decomposition products include aldehydes, alkyl iodides and ethers. It is well known that alcohols other than methanol undergo reductive carbonylation and homologation.

Of the ketones examined (Table 2), methyl ethyl ketone was found to be somewhat stable in long-term operation. Acetone is hydrogenated to isopropanol, whereas cyclopentanone decomposes into numerous unidentified species. The diketones result in low acetaldehyde rates, possibly due to catalyst inhibition via chelation. Esters are known to undergo hydroformylation and homologation [31, 32]. In a reaction carried out with methyl acetate (no methanol) 10 000 psi synthesis gas was consumed, resulting in a mixture composed mainly of ethyl acetate, acetic acid and acetaldehyde. Other esters were not examined due to their hydrolytic instability.

Lastly, it was anticipated that alkanes would be poor solvents because of their low catalyst and water solubilities; however, by increasing the CH₃OH: solvent ratio to 2:1 (by volume) reasonable rates (2 to 4 Mhr^{-1}) and selectivities (~85%) were obtained. There was no indication of decomposition of the alkanes tested; however, in most cases the product mixture contained several phases, making product refining quite difficult.

Of the solvents listed in Table 2, none show a correlation of rate with solvent polarity. This might have been expected due to the postulated intermediacy of cobalt carbonyl anions in the reaction mechanism [16]. The selectivity increase is observed over a wide range of different solvents. As in the case with methanol (no solvent), methyl acetate is the principal byproduct. Methyl acetate probably originates from the reaction of an intermediate acyl-cobalt complex with methanol [33].

$$\begin{array}{c}
O\\
H_2\\
H_2\\
\hline
H_2\\
\hline$$

Reducing the initial methanol concentration by diluting the system with a solvent will favor formation of acetaldehyde; at constant volume the H_2 concentration is relatively unchanged.

(13)

The promotional effect of iodides is generally assumed to be a result of the in situ formation of $CH_{3}I$, which then rapidly reacts with the metal catalyst. In our work we found nearly identical results when charging I₂, HI, CH_{al} or $[CH_{a}PPh_{a}]I$. HI is generated from I_{2} and H_{2} and rapidly reacts with CH₃OH to give CH₃I. In the case of [CH₃PPh₃]I, CH₃I is obtained by the equilibrium

 $[CH_3PPh_3]I \rightleftharpoons CH_3I + PPh_3$

In contrast, low rates were obtained with Group I or II iodides. Addition of Group I or II metal carbonates to a $Co(OAc)_2 \cdot 4H_2O$, I₂ and PPh₃ catalyst mixture had no effect on the activity, ruling out inhibition by the metal cations. These results are in contrast to a phosphine-free cobalt catalyst, for which Group I iodides were reported to be better promoters than I_2 [34].

Little information is available in the literature regarding stress corrosion or pitting of stainless steels by the iodide ion. It has been noted that intense corrosion occurs with most metals upon heating H_2 and I_2 to 370 °C [35]. We have found excessive corrosion rates (>0.01 in per year) with 304, 316, and 317 stainless steel in methanol reductive carbonylation experiments carried out with CoI₂ (0.052 M) at 170 °C and 5000 psi. Similar experiments utilizing PPh₃, *i.e.*, a catalyst consisting of $Co(OAc)_2 \cdot 4H_2O:I_2:PPh_3 = 1:2:2$, CoI₂(PPh₃)₂ or [CH₃PPh₃]₂CoI₄, result in low corrosion rates for 316 (0.002 in per year) and 317 (0.0076 in per year) stainless steel and little, if any, corrosion with Hastelloy C[®]. Excessive corrosion does result if the I₂:PPh₃ molar ratio exceeds 2.0. The mechanism by which PPh₃ inhibits corrosion is not known. Possibilities include (i) formation of a protective coating on the reactor walls (not observed), (ii) stabilization of cobalt complexes which might otherwise be corrosive, or (iii) containing the iodide within the catalytic cycle via reaction of free CH₃I or HI with PPh₃. The fact that the bulk of the iodide is contained within $CoI_2(OPPh_3)_2$ and $[CH_3PPh_3]_2CoI_4$ supports the last notion.

Conclusion

Reductive carbonylation of methanol to acetaldehyde can be carried out with good rates and selectivity using a cobalt/iodide catalyst. The addition of phosphines reduces the corrosivity of the system, and when the ratio of phosphine to iodide is maintained within a controlled range, little effect on the acetaldehyde rate and selectivity is observed. At higher P:I ratios, catalytic activity decreases significantly. When the catalyst components are charged as PR₃ and I₂, a series of reactions occurs which results in the formation of CH₃I, OPR₃ and [MePR₃]I.

Although selectivity to acetaldehyde of 70 - 80% is achieved by the cobalt/iodide/phosphine system in pure methanol, use of a solvent is required to obtain very high selectivities (>90%). The solvent functions primarily as a diluent which retards the reaction of the presumed intermediate cobalt acyl with methanol to form methyl acetate, the major by-product. With the exception of diphenyl ether and alkanes, solvent decomposition becomes a major problem under the reaction conditions employed.

Acknowledgement

We thank Dr. A. Harrison for helpful discussions and Union Carbide for permission to publish this information.

References

- 1 For example see: J. Falbe (ed.), New Syntheses with Carbon Monoxide, Springer, New York, 1980, and references therein.
- 2 B. E. Dale, Ind. Eng. Chem. Prod. Res. Dev., 22 (1983) 466.
- 3 W. Swodenk, Chem. Ing. Tech., 55 (1983) 683.
- 4 I. Wender, R. A. Friedel and M. Orchin, Science, 113 (1951) 206.
- 5 J. Berty and L. Marko, Chem. Tech. (Leipzig), 8 (1956) 260.
- 6 G. Doyle, J. Organometall. Chem., 13 (1981) 237.
- 7 W. R. Pretzer and T. P. Kobylenski, Ann. New York Acad. Sci., 333 (1980) 58.
- 8 M. Röper, H. Loevenich and J. Korff, J. Mol. Catal., 17 (1982) 315.
- 9 G. R. Steinmetz and T. H. Larkins, Organometallics, 2 (1983) 1879.
- 10 A. Deluzarche, G. Jenner, A. Kiennemann and F. A. Erobel Samra, Kohle Erdgass Petrochem., 32 (1979) 436.

- 11 M. E. Fakley and R. A. Head, Appl. Catal., 5 (1983) 3.
- 12 F. A. Cotton, R. D. Barnes and E. J. Bannister, J. Chem. Soc., (1960) 2199.
- 13 N. S. Gill and R. S. Nyholm, J. Chem. Soc., (1959) 3997.
- 14 J. L. Vidal and W. E. Walker, Inorg. Chem., 19 (1980) 896.
- 15 G. S. Koermer and W. E. Slinkard, Ind. Eng. Chem. Prod. Res. Dev., 17 (1978) 231.
- 16 D. W. Slocum, in W. H. Jones (ed.), Catalysis in Organic Chemistry, Academic Press, New York, 1980, p. 245.
- 17 M. Boven, N. Alemdaroglu and J. Penninger, J. Organometall. Chem., 84 (1975) 65.
- 18 M. Arabi, A. Marsonnat, S. Attali and R. Poilbanc, J. Organometall. Chem., 67 (1974) 109.
- 19 M. Bressan, B. Corain, P. Rigo and A. Turco, Inorg. Chem., 9 (1970) 1733.
- 20 M. Bassato, M. Bressan and P. Rigo, J. Organometall. Chem., 232 (1982) 81.
- 21 A. Sacco, Gazz. Chim. Ital., 93 (1963) 542.
- 22 T. Mizoroki and M. Nakayama, Bull. Chem. Soc. Jpn., 38 (1965) 1876.
- 23 T. Mizoroki and M. Nakayama, Bull. Chem. Soc. Jpn., 39 (1966) 1477.
- 24 G. A. Wiley, R. L. Hershkowetz, B. M. Rein and B. C. Chung, J. Am. Chem. Soc., 86 (1964) 964.
- 25 A. V. Bayless and H. Zimmer, Tetrahedron Lett., 35 (1968) 3811.
- 26 T. E. Paxson, C. A. Reilly and D. R. Holecek, J. Chem. Soc., Chem. Commun., (1981) 618.
- 27 R. S. Daroda, J. R. Blackborow and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1980) 1098.
- 28 F. Piacenti and M. Bianchi, in I. Wender and P. Pino (eds.), Organic Synthesis Via Metal Carbonyls, Vol. II, Wiley, New York, 1977, p. 1 and references therein.
- 29 U.S. Pat. 4 339 609 (1982) to Gulf Oil Co.
- 30 U.S. Pat. 4 339 611 (1982) to Gulf Oil Co.
- 31 U.K. Pat. Appl. GB 2 038 329A (1980) to Halcon.
- 32 G. Braca, G. Sbrana, G. Valentini, G. Andrich and G. Gregorio, J. Am. Chem. Soc., 100 (1978) 6238.
- 33 R. W. Johnson and R. G. Pearson, Inorg. Chem., 10 (1971) 2091.
- 34 T. Mizoroki and M. Nakayama, Bull. Chem. Soc. Jpn., 37 (1964) 237.
- 35 V. I. Ginzburg and O. I. Kabakova, Zashcheta Metallov, 5 (1969) 627.