17
Homogeneous Hydrogenation of Carbon Dioxide

Philip G. Jessop

17.1
Introduction

Carbon dioxide (CO_2) fixation for synthetic purposes requires either reduction or coupling reactions. Reduction of CO_2 by catalytic hydrogenation has been extensively studied. Industrial application at present is minor; CO_2 is included with CO in the feed for the currently-practiced heterogeneous hydrogenation to methanol, while Lurgi Öl-Gas-Chemie has explored the hydrogenation of CO_2 without CO as an alternative process [1, 2]. Homogeneously catalyzed hydrogenation of CO_2 is not in production at this time, although it has been 35 years since the first catalysts for the production of formamides were discovered by Haynes and coworkers [3, 4]. During the past 15 years, much more efficient catalysts have been developed; before 1990, the only system to give high yields of formic acid (>1 000 TON) operated at 160 °C [5], but now a catalyst giving 32 000 TON at only 50 °C is known [6]. Even greater improvements have been observed for the synthesis of formamides by CO_2 reduction. Unfortunately, the same progress has not been observed for homogeneously catalyzed hydrogenation of CO_2 to other products such as methanol or oxalic acid.

This chapter presents an overview of the primary findings from 1970 to the present. Hydrogenation using H_2 as the reductant will be described, although there are examples of the electrocatalytic reduction of CO_2 [7–10] and the use of other reductants [11]. More detailed reviews on homogeneous hydrogenation of CO_2 have been published, covering the years up to 1994 [12, 13] and from 1995 to 2003 [14].

The motivation for studying or contemplating industrial applications of CO_2 hydrogenation does not stem from a desire to use up excess CO_2 in order to lessen global warming. If the H_2 that is used in the reduction is derived from either the water-gas shift reaction (WGSR) or from steam reforming of methane, then 1 or 0.25 equivalents of CO_2, respectively, were produced per molecule of H_2. Thus, the hydrogenation of CO_2 to formic acid, using H_2 from WGSR, results in neither a net consumption nor a net production of CO_2. Hy-

	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° J/(mol•K)
$CO_2(g) + H_2(g) \rightleftharpoons HCO_2H(l)$	32.8	-31.5	-216
$CO_2(g) + H_2(g) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	-9.5	-84.3	-250
$CO_2(g) + H_2(g) + NHMe_2(liq) \rightleftharpoons HC(O)NMe_2(liq) + H_2O(l)$	na	-239	na
$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(l) + H_2O(l)$	-9.5	-131	-409

Scheme 17.1 The thermodynamics of CO_2 reductions.

drogenation of CO_2 to formic acid using H_2 from methane does result in the net consumption of CO_2, but in order to consume a significant portion of the excess CO_2 one would have to synthesize a ridiculously large amount of formic acid!

Multiple products are possible from CO_2 hydrogenation, but all of the products are entropically disfavored compared to CO_2 and H_2 (Scheme 17.1). As a result, the reactions must be driven by enthalpy, which explains why formic acid is usually prepared in the presence of a base or another reagent with which formic acid has an exothermic reaction. Of the many reduction products that are theoretically possible, including formic acid, formates, formamides, oxalic acid, methanol, CO, and methane, only formic acid and its derivatives are readily prepared by homogeneous catalysis.

17.2
Reduction to Formic Acid

Formic acid, a synthetic precursor and a commercial product for use in the leather, agriculture and dye industries, is traditionally prepared by carbonylation of NaOH at elevated pressure and temperature [15, 16]. The use of toxic CO begs the question; can a competitive route be found using CO_2 instead? Given that CO and H_2 are roughly interchangeable thanks to the WGSR and that CO_2 in the post-Kyoto world is essentially free, CO_2/H_2 should be competitive with CO if sufficiently active and inexpensive catalysts can be identified. Of course, the economics are considerably more complicated than that simple analysis: complicating factors include the costs of water addition or removal and the costs of the bases used. Nevertheless, the homogeneous hydrogenation of CO_2 as an alternative route to formic acid has been the subject of a large number of studies, starting with the first reports in the mid-1970s [17, 18].

Hydrogenation of CO_2 to formic acid (Eq. (1)) is thermodynamically unfavorable unless a base is present (see Scheme 17.1); the proton transfer to the base drives the reaction. In the absence of a base, the reaction usually fails completely or provides only small yields [19, 20], even though the initial rate of reaction was high in one case [21]. For the reaction in water, NaOH, bicarbonates, carbonates and even dialkylamines [22] are used as the base. For the reaction in or-

ganic solvents, amines are most commonly used, but some amines are decidedly superior to others in this respect. Whilst NEt$_3$ is most often used because it is inexpensive, far greater rates are observed (at least for the RuCl(OAc)(PMe$_3$)$_4$-catalyzed hydrogenation) if an amidine or guanidine base such as 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) is used instead [6]. The increase in rate with some bases has never been satisfactorily explained, but could be related to a base-assisted step in the mechanism (e.g., a hydrogen-bonding interaction between metal-bound H$_2$ and base during hydrogenolysis of a metal formate; see Section 17.2.1) or possibly to the ability of amidine bases to solubilize CO$_2$ in the form of bicarbonate in wet organic solvents [23]. Whichever base is used, there remains the question of how to separate the base from the formic acid product. The addition of an acid to the raw amine/formic acid mixture would liberate the formic acid and leave the amine in the form of a salt [24]. A base-exchange [25, 26] with a high-boiling amine such as imidazole would allow for thermal decomposition of the salt to give free formic acid and recyclable amine [27, 28].

$$CO_2 + H_2 \rightleftharpoons HCO_2H \tag{1}$$

The equilibrium yield of formic acid is limited by the amount of base. Many reports describing the hydrogenation in aqueous solution indicate yields of up to 1 mol formic acid per mol base, although Karakhanov was able to obtain 1.34 mol per mol NHEt$_2$ in water at 155 °C [29]. Higher yields of 1.6 to 1.9 are found for the reaction in organic solvents [18] and in supercritical CO$_2$ (scCO$_2$) [30, 31]. Because the reaction in the absence of base is thermodynamically unfavorable, added base must still stabilize the formic acid product, even after 1 equiv. acid has been produced and essentially all of the base is protonated. In fact, HCO$_2$H and NEt$_3$ are known [32–34] to exist in relatively stable adducts of various ratios, including 1:1, 2:1, and 3:1, plus unprotonated amine (even at 3:1 acid:amine ratios) and oligomeric chains of formic acid molecules ending with an amine. It is not clear, given that these higher ratios are possible, why the yield in practice is limited to a ratio of 1.9:1, or lower.

Solvent choice is important for optimizing the rate of this reaction. One of the most active catalysts to date, RhCl(TPPTS)$_3$, is used in water, despite the very poor solubility of H$_2$ in that medium. For the hydrophobic catalysts, the best solvents so far have been scCO$_2$ and polar aprotic solvents. The supercritical medium is highly effective because of the enormous concentrations of CO$_2$ and H$_2$ in the same phase as the catalyst, and also the elimination of mass-transfer limitations on the transfer of these reagent gases into traditional liquid solvents. These advantages are particularly important for the RuH$_2$(PMe$_3$)$_4$ and RuCl(OAc)(PMe$_3$)$_4$ catalyst precursors [30, 31, 35] because the hydrogenation rate is first order with respect to both H$_2$ and CO$_2$ [36]. For the same catalysts in conventional liquid solvents, the rate was found to decrease in the order DMSO > MeOH > MeCN > THF > H$_2$O. Performing the reaction in MeOH/NEt$_3$ and diluting the solvent with hexane causes the rate to decrease, a result which was attributed to the

decrease in the dielectric constant of the medium [36]. Similarly, dissolving large amounts of ethane or fluoroform (CHF_3) into the MeOH/NEt_3 mixture causes the rate to drop or rise, respectively [36]. Rhodium(I) catalyst precursors [20, 37] have similar dependence of rate on solvent polarity, with DMSO always being excellent and less-polar aprotic solvents such as acetone, THF, or benzene being inferior. However, methanol was found to be better than DMSO for $RhCl(PPh_3)_3$ [37] and decidedly inferior for $[RhCl(COD)]_2$/dppb [20]. The overall need for a highly polar solvent is not related to gas solubility (H_2 is more soluble in the nonpolar solvents), but may be related to the ability of polar solvents such as DMSO to increase the entropy of the formic acid product by disrupting hydrogen bonding [20].

Even in aprotic solvents, the hydrogenation with most catalysts requires at least a small quantity of water or an alcohol as a co-catalyst or promoter; using thoroughly dried solvents leads to poor rates of reaction. This phenomenon was first observed by Inoue et al. [18] for $Pd(dppe)_2$, but has since been found to exist also for many of the Rh- and Ru-based catalysts. However, for the catalyst precursor $[RhCl(COD)]_2$/dppb, added water was found to inhibit the hydrogenation, and added molecular sieves to remove trace water were found to help the rate [20]. For those systems which require water, the amount needed is typically very small; on the order of a few equivalents per catalyst [6, 18]. There are so many possible roles for water in a hydrogenation mechanism that it is very difficult to demonstrate conclusively how the water may be helping. Possibilities include hydrogen bonding during CO_2 insertion, hydrolysis of formate ligands, capturing CO_2 in the form of bicarbonate, or even supplying protons in an ionic hydrogenation. Some alcohols can be more effective than water at promoting the reaction. Munshi et al. [6] surveyed a large number of alcohols as co-catalysts for the $RuCl(OAc)(PMe_3)_4$ and found the most effective alcohols to be those that have an aqueous-scale pK_a below that of the protonated amine (10.7 for $HNEt_3^+$) and that have a potentially coordinating conjugate base. Thus, 3,5-$(CF_3)_2C_6H_3OH$ and triflic acid, which fulfill both requirements, are particularly effective, whereas MeOH and water are only moderately active because they are insufficiently acidic, and 2,6-$tBu_2C_6H_3OH$ and HBF_4 have no activity because their conjugate bases are too sterically encumbered or insufficiently nucleophilic to have any coordinating ability.

A large number of catalysts or catalyst precursors for the reaction in Eq. (1) have been identified (Table 17.1). Almost all of these are complexes of Rh and Ru, although there are a few, less active, examples of Ir, Pd, Ni, Fe, Ti, and Mo. The most active catalysts are $RhCl(TPPTS)_3$, $Rh(hfacac)(dcpb)$ and $RuCl(OAc)$ $(PMe_3)_4$, with little difference between them after rough correction of the turnover frequencies (TOF) for pressure and temperature differences [38]. Musashi and Sakaki [39] argue that the barrier to CO_2 insertion into M–H bonds increases in the order Rh(I) < Ru(II) < Rh(III) because Rh(III)–formate bonds are too weak and Ru(II)–H bonds are too strong compared to the case of Rh(I).

Table 17.1 Homogeneous catalyst precursors for the hydrogenation of CO_2 to formic acid.

Catalyst precursor	Base	$P_{H2, CO2}$[a] [atm]	Temperature [°C]	Time [h]	TON	TOF[b] [h^{-1}]	Reference(s)
Ruthenium							
$Ru_2(CO)_5(dppm)_2$	NEt$_3$	38, 38	RT	21	2160	103	40
RuCl$_3$, PPh$_3$	NEt$_3$	60, 60	60	5	200	40	41
RuH$_2$(PPh$_3$)$_4$	NEt$_3$	25, 25	RT	20	87	4	18
RuH$_2$(PPh$_3$)$_4$	Na$_2$CO$_3$	25, 25	100	4	169	42	42
RuH$_2$(PMe$_3$)$_4$	NEt$_3$	85, 120	50	1	1400	1400	30
RuCl$_2$(PMe$_3$)$_4$	NEt$_3$	80, 140	50	47	7200	153	31
RuCl(OAc)(PMe$_3$)$_4$	NEt$_3$	70, 120	50	0.3	32 000	95 000	6
TpRuH(PPh$_3$)(CH$_3$CN)	NEt$_3$	25, 25	100	16	1815	113	43, 44
[Ru(Cl$_2$bpy)$_2$(H$_2$O)$_2$][O$_3$SCF$_3$]$_2$	NEt$_3$	30, 30	150	8	5000	625	45
[(C$_5$H$_4$(CH$_2$)$_3$NMe$_2$)Ru(dppm)]BF$_4$	None	40, 40	80	16	8	0.5	46
[RuCl$_2$(CO)$_2$]$_n$	NEt$_3$	81, 27	80	0.3	400	1300	24
K[RuCl(EDTA-H)]	None	3, 17	40	0.5	na	250	21
[RuCl$_2$(TPPMS)$_2$]$_2$	NaHCO$_3$	60, 35	80	0.03	320	9600	**47**
[RuCl(C$_6$Me$_6$)(DHphen)]Cl	KOH	30, 30	120	24	15 400	642	48
CpRu(CO)(μ-dppm)Mo(CO)$_2$Cp	NEt$_3$	30, 30	120	45	43	1	49
Rhodium							
[RhCl(COD)]$_2$+dppb	NEt$_3$	20, 20	RT	22	1150	52	25
[RhCl(COD)]$_2$+dippe	NEt$_3$	40 total	24	18	205	11	50
[RhH(COD)]$_4$+dppb	NEt$_3$	40 total	RT	18	2200	122	20
RhCl(PPh$_3$)$_3$	Na$_2$CO$_3$	60, 55	100	3	173	58	51
RhCl(PPh$_3$)$_3$	NEt$_3$	20, 40	25	20	2700	125	37
RhCl(TPPTS)$_3$	NHMe$_2$	20, 20	81	0.5		7260	22, 52
[RhCl(η^2-CYPO)$_2$]BPh$_4$	NEt$_3$	25, 25	55	4.2	420	100	53
Rh(hfacac)(dcpb)	NEt$_3$	20, 20	25	–	–	1335	54
[Rh(NBD)(PMe$_2$Ph)$_3$]BF$_4$	None	48, 48	40	48	128	3	19
RhCl$_3$+PPh$_3$	NHMe$_2$	10, 10	50	10	2150	215	29
Palladium							
Pd(dppe)$_2$	NEt$_3$	25, 25	110	20	62	3	18
Pd(dppe)$_2$	NaOH	24, 24	RT	20	17	0.9	55
PdCl$_2$	KOH	110, na	160	3	1580	530	5
PdCl$_2$(PPh$_3$)$_2$	NEt$_3$	50, 50	RT	na	15	na	26

Table 17.1 (continued)

Catalyst precursor	Base	$P_{H2, CO2}$[a] [atm]	Tempera-ture [°C]	Time [h]	TON	TOF[b] [h^{-1}]	Reference(s)
Other metals							
$TiCl_4/Mg$	None	1, 1	RT	na	15	na	17
$Ni(dppe)_2$	NEt_3	25, 25	RT	20	7	0.4	18
$NiCl_2(dcpe)$	DBU	40, 160	50	216	4400	20	56
$FeCl_3/dcpe$	DBU	40, 60	50	7.5	113	15	56
$MoCl_3/dcpe$	DBU	40, 60	50	7.5	63	8	56
[Cp*IrCl(DHphen)]Cl	KOH	30, 30	120	10	21 000	2100	48

a) In some cases, the pressure of CO_2 was not given and was calculated from the total stated pressure minus the pressure of H_2.
b) The TOF values are not directly comparable to each other because some are at complete conversion and some are at partial conversion. They can, however, give an order of magnitude indication. Initial TOF values will be even higher.
na = data not available; RT = room temperature.

17.2.1
Insertion Mechanisms

Carbon dioxide is known to readily insert into a metal–hydride bond to give a metal formate [57, 58]; this forms the first step in insertion mechanisms of CO_2 hydrogenation (Scheme 17.2). Both this insertion step and the return path from the formate complex to the hydride, generating formic acid, have a number of possible variations.

Insertion of CO_2 into a metal–hydride bond normally requires the prior dissociation of an ancillary ligand to generate a coordinatively unsaturated complex, because CO_2 coordination to the metal usually precedes the formal insertion (Scheme 17.3, lower pathway). *Ab initio* calculations [59] support this mechanism for the insertion of CO_2 into the Ru–H bond of $RuH_2(PH_3)_4$, a model for the catalyst $RuH_2(PMe_3)_4$. However, it is theoretically possible for CO_2 insertion to take place without prior CO_2 coordination (Scheme 17.3, upper pathway) [60, 61]. The
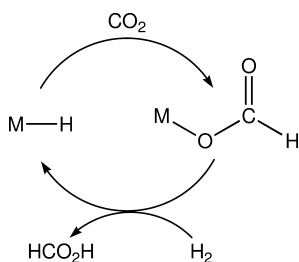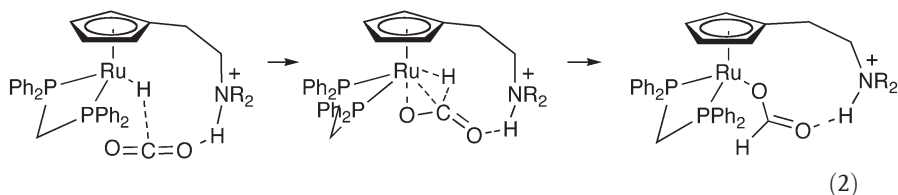

**Scheme 17.2** Simplified insertion mechanism.
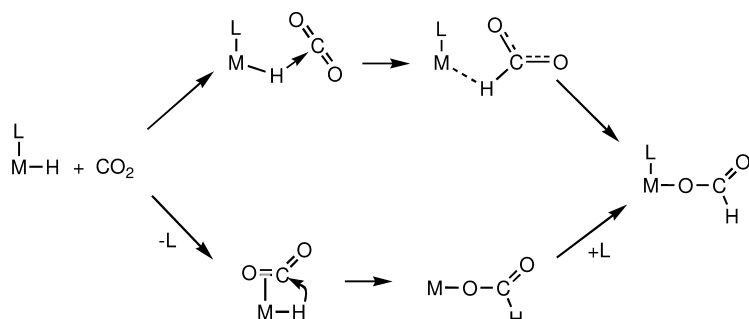
Scheme 17.3 Mechanisms of CO$_2$ insertion into a metal-hydrogen bond. "L" represents a potentially dissociable ligand. Ancillary ligands are not shown.

upper pathway of Scheme 17.3 was supported for the CO$_2$ insertion step of the catalyst in Eq. (2) by hybrid density functional calculations [62, 63].

$$(2)$$

Hydrogen-bonding during the CO$_2$ insertion step may bring down the kinetic barrier and thereby explain the promoting effect of water and alcohols. Tsai and Nicholas [19] first proposed this for their system based on the catalyst precursor [Rh(nbd)(PMe$_2$Ph)$_3$]BF$_4$ (Scheme 17.4a). However, for the insertion of CO$_2$ into the Rh–H bonds of [RhH$_2$(PH$_3$)$_2$(H$_2$O)]$^+$ and [RhH$_2$(PH$_3$)$_3$]$^+$, proposed to be models of the actual catalyst in Tsai and Nicholas' system, Musashi and Sakaki's calculations [39] show that for this particular system the barrier-lowering effect of water during the attack of CO$_2$ is due not to hydrogen-bonding but to differing trans effects present in the complexes with and without water. In contrast, for the TpRuH(PPh$_3$)(MeCN) system, hydrogen-bonding to external water was proposed (Scheme 17.4b). Density functional theory (DFT) calculations suggest that this interaction reduces the transition state energy by only 23 kJ mol^{-1} [43].

a)

b)
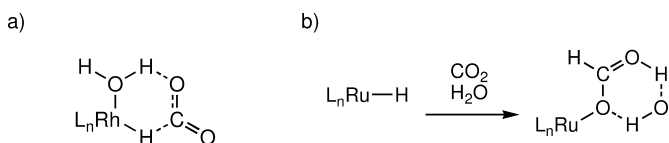
Scheme 17.4 Possible hydrogen-bonding interactions assisting in the insertion of CO$_2$ for the (a) [Rh(nbd)(PMe$_2$Ph)$_3$]BF$_4$ [19] and (b) TpRuH(PPh$_3$)(MeCN) systems.

The hydrogen-bonding interaction in Eq. (2) greatly decreases the activation energy for CO_2 insertion [62, 63].

The formate complex that results from CO_2 insertion can liberate formic acid and return to the starting hydride species by one of three return pathways, the most obvious of which is hydrogenolysis (path A of Scheme 17.5). Hydrogenolysis involves either oxidative addition of H_2 or coordination of H_2 as a molecular hydrogen ligand, followed by elimination of formic acid, although technically it is possible for hydrogenolysis via a "sigma-bond metathesis" mechanism without prior H_2 coordination. Evidence for the hydrogenolysis mechanism for the intermediate $[M(O_2CH)(CO)_5]^-$ (M = Cr, W) was the fact that the related carboxylate species $[M(O_2CMe)(CO)_5]^-$ reacts with MeOH to form $MeCO_2Me$ only when H_2 is present [64]. In that system, H_2 was believed to bind to a site made available by prior dissociation of a carbonyl ligand. The hydrogenolysis pathway was also proposed for the catalytic intermediate $Rh(O_2CH)(dppb)$; the dihydride formed by H_2 oxidative addition was calculated to be lower in energy than the molecular hydrogen complex, but the latter was more reactive and therefore was the dominant pathway [65, 66]. The reaction between the bound H_2 ligand and formate was facilitated by a hydrogen-bonding interaction with external base (Scheme 17.6 b). For some systems, the H atom from the H_2 ligand might transfer to the free carbonyl oxygen atom by a six-center transition state (Scheme 17.6 c) rather than to the metal-bound oxygen via a four-center transition state (Scheme 17.6 a). The six-membered transition state was shown, by calculation, to be preferred for the Ru intermediate $[RuH(O_2CH)(H_2)(PR_3)_3]^+$ [59].

Path B in Scheme 17.5 involves hydrolysis or alcoholysis of the formate complex, yielding formic acid and a hydroxide or alkoxide complex, which then undergoes hydrogenolysis. This pathway would explain the observations that water
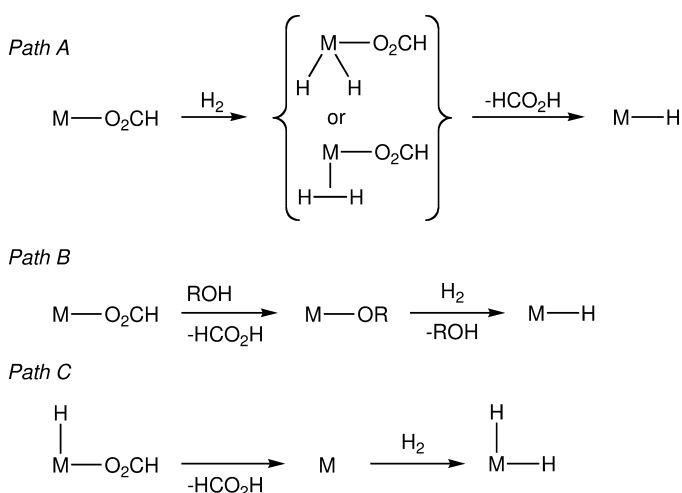
Scheme 17.5 Return pathways from the formate intermediate to the starting hydride.
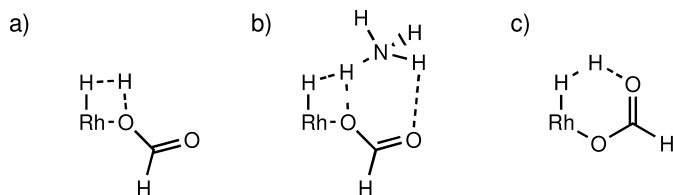
Scheme 17.6 Transition states for the transfer of a hydrogen atom from a molecular hydrogen ligand to a formate ligand: a) four-centered; b) four-centered and base-assisted [66]; and c) six-centered [59].

and alcohols increase the rate of reaction for many catalysts. Inoue et al. [18] proposed this mechanism for the reaction catalyzed by Pd(dppe)$_2$ for precisely this reason. Further, it has been observed for the RuCl(OAc)(PMe$_3$)$_4$ catalyst precursor that the most effective alcohols are those for which the conjugate bases are not sterically encumbered (and therefore are potentially coordinating) [6], although none of these arguments can be considered to be more than circumstantial.

Path C (Scheme 17.5), which involves reductive elimination of formic acid before reaction with H$_2$, is only possible for dihydride and polyhydride catalysts. This pathway was proposed for the catalyst precursor [Rh(nbd)(PMe$_2$Ph)$_3$]$^+$ by Tsai and Nicholas [19], who observed the intermediates [RhH$_2$(PMe$_2$Ph)$_3$L]$^+$ and [RhH(η^2-O$_2$CH)(PMe$_2$Ph)$_2$L]$^+$ (L=H$_2$O or solvent).

17.2.2
Ionic Hydrogenation

Ionic hydrogenation mechanisms involve the sequential transfer of hydride and proton to the substrate [67]. This was suggested by the Leitner group for the hydrogenation of CO$_2$ with the catalyst precursor RhH(dppp)$_2$ (Scheme 17.7) [50]. Spectroscopic evidence for each of the three intermediates was obtained by studying the steps as stoichiometric reactions. However, catalyst precursors that generate the highly active RhH(diphosphine) species in solution were subsequently found to operate by a more conventional insertion mechanism [20].
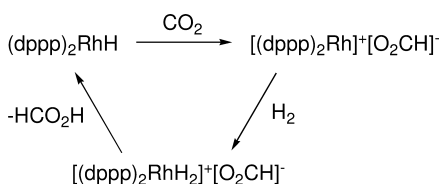
Scheme 17.7 An ionic hydrogenation mechanism for CO$_2$ hydrogenation [50].

17.2.3
Concerted Ionic Hydrogenation

The Noyori mechanism for the concerted ionic hydrogenation of ketones involves the simultaneous donation of a hydride ion from a metal hydride complex and a proton from an acidic ligand bound to the same metal (Scheme 17.8a). There is no reason why this mechanism should not also be possible for CO_2 hydrogenation (Scheme 17.8b) [6, 43, 68], although it has not yet been possible to demonstrate that this mechanism operates for any of the catalysts shown in Table 17.1. The mechanism does not require the ketone or CO_2 to bind to the metal or to insert into the M–H bond, as is required in more conventional mechanisms. Pomelli et al. [68] evaluated the possibility that bound formic acid could serve as the proton source in such a mechanism for RhH(diphosphine) catalyst, but found that the energy of the intermediates in the conventional insertion pathway were lower. The concerted mechanism for CO_2 hydrogenation was more recently suggested by Lau's group [43, 44] to explain the catalytic activity of the complex TpRuH(-MeCN)(PPh$_3$) in the presence of water, methanol and the acidic alcohol CF_3CH_2OH, the last of which offers the greatest rates of reaction. NMR spectroscopy detected TpRu(OCH$_2$CF$_3$)(PPh$_3$)(MeCN) and possibly TpRu(O$_2$-COCH$_2$CF$_3$)(PPh$_3$)(MeCN). The ionic hydrogenation mechanism does not necessarily require an inner-sphere alcohol ligand. The alcohol could merely be outer-sphere, bound by an unconventional hydrogen bond to the metal hydride (i.e., M–H$\cdots$HOR). Hybrid density functional calculations have shown that the transfer of H_2 from an unconventional hydrogen bond to CO_2 is energetically feasible [63].

17.2.4
Bicarbonate Hydrogenation

In basic aqueous solutions, CO_2 exists primarily in the bicarbonate or carbonate forms. Thus, the hydrogenation of either CO_2 or bicarbonate salts in such solutions could conceivably proceed by hydrogenation of the bicarbonate anion. Pd
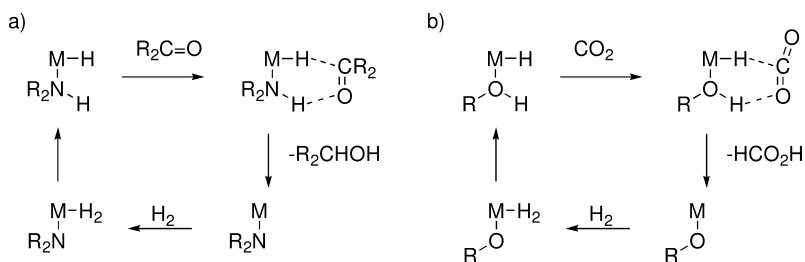
Scheme 17.8 Concerted ionic hydrogenation mechanisms for the hydrogenation of (a) ketones and (b) CO_2. The acidic ligand is shown as an alcohol in Scheme 17.7b, but could equally well be water, a secondary amine, or a carboxylic acid.

complexes are known [5, 18] to catalyze the hydrogenation of bicarbonates and carbonates, although the mechanism is unknown. This mechanism has been proposed for the catalyst precursors $PdCl_2/KOH$ [5, 69], $RuCl_2(PTA)_4$ [70], and $[RuCl_2(TPPMS)_2]_2$ [47]. The complex $RuCl_2(PTA)_4$ hydrogenates CO_2 rapidly in basic aqueous solutions but not in the absence of base, although this may be due to thermodynamics rather than evidence of a bicarbonate hydrogenation mechanism. Reaction of $RuCl_2(TPPMS)_2$ with $NaHCO_3$ gives $Ru(O_3CH)_2(TPPMS)_2$, which reacts stoichiometrically with H_2 to produce HCO_2^-.

It must keep be borne in mind that insertion and other pathways for CO_2 hydrogenation are not only possible but are believed to operate for some catalyst precursors, such as $RhCl(TPPTS)_3$, even in aqueous solutions [52].

17.2.5
Other Mechanisms

Hydrogenation of CO_2 to formic acid could potentially proceed first by reduction to CO, followed by a reaction between CO and water to give formic acid, a reaction which is known (Eq. (3)). It is unlikely that this pathway to formic acid is common because very few homogeneous catalysts (primarily homoleptic carbonyl complexes) [71–73] have been reported for the hydrogenation of CO_2 to CO, and because the few CO_2 hydrogenation catalysts that have deliberately been exposed to CO, in order to check whether this pathway is operating, have been poisoned as a result [18, 19, 31, 74].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \rightleftharpoons HCO_2H \qquad (3)$$

17.3
Reduction to Oxalic Acid

Hydrogenation of CO_2 could also generate oxalic acid (Eq. (4)); the electrochemical reduction of CO_2 to oxalate dianion has been well studied [75–77]. However, there have been almost no reports of oxalic acid or its esters being detected among the products of homogeneous CO_2 hydrogenation. Denise and Sneeden [78] reported the detection of traces of diethyloxalate (0.002 TON) in a similar reaction in ethanol solvent at 120 °C. The lack of other reports may not necessarily be evidence that oxalic acid is not formed; the conventional methods for detecting formic acid (especially ^{1}H-NMR spectroscopy) are not effective for oxalic acid. Therefore, oxalic acid – were it formed – would go undetected by many researchers studying the hydrogenation of CO_2 to formic acid. In order to determine whether oxalic acid is a co-product of formic acid production, a method was developed in the Jessop group which used dimethylsulfate to methylate the oxalate anion. The dimethyloxalate was then detectable by gas chromatography. By using this assay method, it was possible to show that catalysts having

high activity for the hydrogenation of CO_2 to formate anion do not simultaneously produce detectable quantities of oxalate anion [79].

$$2CO_2 + H_2 \rightleftharpoons HO_2CCO_2H \tag{4}$$
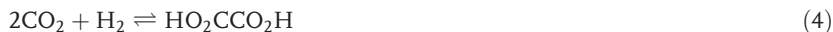
It may not be that surprising that an effective homogeneous catalyst for the reaction shown by Eq. (4) has not been found; it is difficult to imagine a facile mechanism by which oxalate anion or oxalic acid could be generated at a metal center.
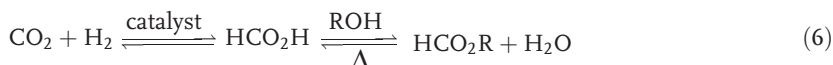
17.4
Reduction to Formate Esters

17.4.1
In the Presence of Alcohols

Formate esters can be synthesized by the hydrogenation of CO_2 in the presence of alcohols in addition to the usual base (Eq. (5) and Table 17.2). The alcohol used is typically methanol or ethanol, giving methyl- or ethylformate; the yield decreases with increasing length of the alkyl chain [80, 81]. Most typically, the pathway is catalytic hydrogenation of CO_2 to formic acid followed by an uncatalyzed thermal esterification (Eq. (6)). The formic acid intermediate, which has been observed spectroscopically for the $RhCl(PPh_3)_3$ [80] and $RuCl_2(PMe_3)_4$ [82] systems, builds up to a concentration somewhat lower than 1 : 1 with the base. The thermal esterification is slow because the reaction is performed in the presence of excess base. Tests of thermal esterification under basic conditions have been performed separately; acetic acid is esterified, in 25% yield after 44 h at 100 °C, by an excess of methanol in the presence of 1 equiv. NEt_3 [31]. The yield of methyl formate from CO_2 is optimum at a temperature which is sufficiently high to allow substantial esterification, but not so high that the hydrogenation catalyst is deactivated. This optimum temperature is ~80 °C for the $RuCl_2(PMe_3)_4$ catalyst precursor [31, 82] and 100–125 °C for the $RhCl(PPh_3)_3$ [80]. Selectivity, on the other hand, is poor at the optimum temperature but greater at higher temperatures, where the yield is poor instead [31, 82]. Complete selectivity is not obtained in the presence of base, although Lodge and Smith [83] showed that the liquid products obtained after the reaction in the presence of basic Al_2O_3 contained only the ester and no formic acid; presumably the acid was captured by the solid base.

$$CO_2 + H_2 + ROH \rightleftharpoons HCO_2R + H_2O \tag{5}$$

$$CO_2 + H_2 \xrightleftharpoons{\text{catalyst}} HCO_2H \xrightleftharpoons[\Delta]{ROH} HCO_2R + H_2O \tag{6}$$

Formate ester synthesis by CO_2 hydrogenation in the absence of base has also been observed [45, 64, 74, 84]. As one might expect, the selectivity is much

Table 17.2 Homogeneous catalyst precursors for the hydrogenation of CO_2, in the presence of methanol or ethanol, to the corresponding formate esters.

Catalyst precursor	Base	$P_{H2, CO2}$[a] [atm]	Temperature [°C]	Time [h]	TON	TOF[b] [h^{-1}]	Reference(s)
Ruthenium							
$Ru_4H_3(CO)_{12}^-$	None	17, 17	125	24	7	0.3	74
$RuHCl(PPh_3)_3/BF_3$	None	30, 30	100	na	17	na	86
$RuCl_2(PPh_3)_3$	Al_2O_3	60, 20	100	64	470	7.3	83
$RuCl_2(PMe_3)_4$	NEt_3	80, 125	80	64	3500	55	82
$[Ru(Cl_2bpy)_2(H_2O)_2][O_3SCF_3]_2$	NEt_3	30, 30	100	8	160	20	45
*$RuCl_2(dppe)_2$	NEt_3	85, 130	100	16	12 900	830	87
$TpRuH(PPh_3)(MeCN)$	NEt_3	25, 25	100	16	75	4.7	44
Rhodium							
$RhCl(PPh_3)_3$	NEt_3	25, 25	140	21	30	1.4	81
$RhCl(PPh_3)_3$	NaOMe	68, 29	140	21	27	1.3	55
$RhCl(PPh_3)_3$	TED	>200, 48	100	5	120	24	80
Palladium							
$Pd(dppe)_2$	NEt_3	25, 25	140	21	24	1.1	81
$Pd(dppm)_2$	NEt_3	70, 30	160	21	58	2.8	88
$Pd(dppm)_2$	NEt_3	15, 15	120	24	9	0.4	89, 90
$MnPdBr(CO_3)(dppm)_2$	NEt_3	6, 6	130	na	na	7	91
Other metals							
$Fe_3H(CO)_{11}^-$	None	20, 20	175	96	6	0.06	84
$W(O_2CH)(CO)_5^-$	None	17, 17	125	24	16	0.7	64
$IrH_3(PPh_3)_3/BF_3$	None	30, 30	100	na	38	na	86

a) In some cases, the pressure of CO_2 was not given and was calculated from the total stated pressure minus the pressure of H_2.

b) The TOF values are not directly comparable to each other because some are at complete conversion and some are at partial conversion. They can, however, give an order of magnitude indication. Initial TOF values will be even higher.

na = data not available.

greater by this method because there is no base to interfere with the esterification or to stabilize the formic acid intermediate. Although there have not yet been reports of very high TON by this method, the value of 160 obtained by Lau and Chen using the $[Ru(Cl_2bpy)_2(H_2O)_2][O_3SCF_3]_2$ precursor is the most impressive [45].

Other mechanisms for the synthesis of alkylformates, not via formic acid esterification, are possible. Hydrogenation of CO_2 to CO, followed by catalytic carbonylation of alcohol, would produce alkyl formate. This mechanism seems more likely for the anionic metal carbonyls because they are known catalysts for alcohol carbonylation. However, Darensbourg and colleagues [64, 74, 85] showed

that $[W(O_2CH)(^{13}CO)_5]^-$ gives $H^{12}CO_2H$ as a product, and they proposed that formic acid was again the intermediate for the $[MH(CO)_5]^-$ (M = Cr, W) system, even though formic acid was not directly observed in the presence of alcohol. Another possible mechanism is the hydrogenation of alkyl carbonate anion formed by the reaction of alcohol, amine, and CO_2, although to date there are no known examples of this mechanism. Finally, alcoholysis of a metal formate complex to give a metal hydroxide and alkyl formate (Eq. (7), in contrast to path B in Scheme 17.5), was proposed by Kolomnikov et al. [86]. However, Darensbourg showed that this mechanism could be ruled out for $[M(O_2CH)(CO)_5]^-$ because that complex does not react with alcohol [64].

$$MO_2CH + ROH \rightleftharpoons MOH + RO_2CH \tag{7}$$

17.4.2
In the Presence of Alkyl Halides

Given the lack of reactivity of higher alcohols in this reaction, alternative means of producing alkylformates have been explored using more reactive reagents instead of alcohols. Alkyl halides have been known, since Kolomnikov's 1972 study [86], to produce alkyl formates when they are present during CO_2 hydrogenation (Eq. (8)). That study described the production of methyl formate from methyl iodide in very low yield and only 5 TON using Ru, Ir, and Os phosphine complexes. Better yields (up to 64% but only 15 TON) were obtained by Darensbourg and Ovalles [92] using $[Cr_2H(CO)_{10}]^-$ or $[WCl(CO)_5]^-$ catalyst precursors and NaO_2COH or NaOMe as base. The base was necessary to trap the HX acid. The proposed mechanism is shown in Scheme 17.9. The last step of the mechanism, the reaction of bound RCl with a formate ligand, was investigated kinetically and is proposed to proceed by oxidative addition of the RCl followed by reductive elimination of the formate ester. Alkyl chlorides were found to be more reactive than the bromides or iodides because the heavier halides led to excessive stability of the catalytic intermediate $[MX(CO)_5]^-$. Bulky alkyl halides react
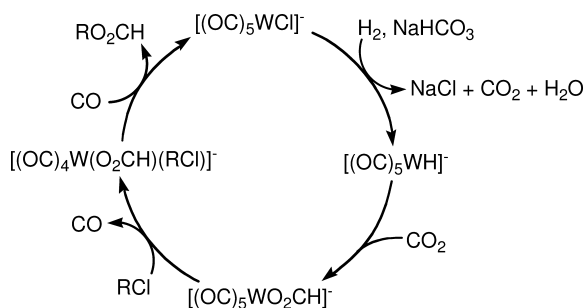
Scheme 17.9 Proposed mechanism for the preparation of formate esters using alkyl halides [92].

slowly, or not at all. Yields would have been better had there not been production of alcohol by formate ester hydrolysis and production of alkane by a side reaction (Eq. (9)).

$$H_2 + CO_2 + RX \rightleftharpoons RO_2CH + HX \qquad (8)$$

$$[MH(CO)_5]^- + RX \rightleftharpoons [MX(CO)_5]^- + RH \qquad (9)$$

17.4.3
In the Presence of Epoxides

Hydrogenation of carbon dioxide in the presence of an epoxide generates a mixture of the diol, its formate esters, and the cyclic carbonate. While the reaction has been shown to operate in high yield (1300 TON for the cyclic carbonate; Eq. (10)) [93], the fact that a mixture is generated and that the cyclic carbonate could be made more cleanly in the absence of H_2 makes the reaction uninteresting for synthesis. Sasaki's group showed that this reaction in the presence of an amine base gives CO rather than cyclic carbonate (Eq. (11)) [94]. The epoxide then serves as a trap for the water.


(10)

(11)
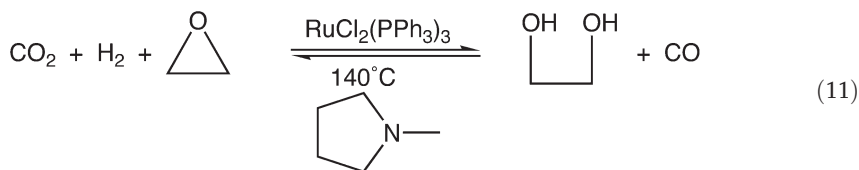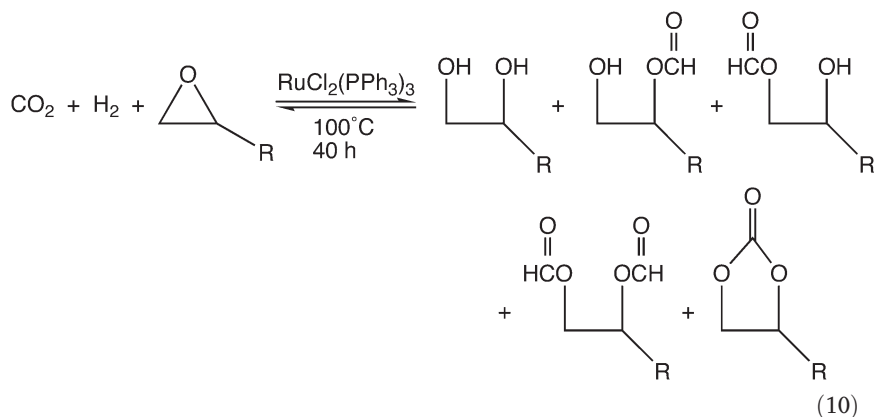
17.5
Reduction to Formamides

Formamides have applications as solvents (particularly dimethylformamide (DMF) and formamide itself), as intermediates for insecticides and pharmaceuticals, and (for formanilide, PhNHC(O)H) as an antioxidant [95]. Formamides are prepared either from CO or from methylformate or formamide, which are themselves prepared from CO.

Preparation of formamides from CO_2 and a non-tertiary amine by homogeneous hydrogenation has been well studied and is extremely efficient (Eq. (12)). Essentially complete conversions and complete selectivity can be obtained (Table 17.3). This process seems more likely to be industrialized than the syntheses of formic acid or formate esters by CO_2 hydrogenation. The selectivity is excellent, in contrast to the case for alkyl formates, because the amine base which would stabilize the formic acid is used up in the synthesis of the formamide; consequently little or no formic acid contaminates the product. The only byproducts that are likely to crop up in industrial application are the methylamines by over-reduction of the formamide. This has been observed [96], but not with such high conversion that it could constitute a synthetic route to methylamines.

$$CO_2 + H_2 + NHR_2 \rightleftharpoons HC(O)NR_2 + H_2O \tag{12}$$
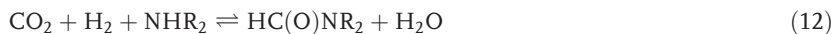
The formamide that has most often been synthesized in studies of this reaction is DMF. The first report of the reaction was by Haynes et al. in 1970 [3]. By far the most active catalyst precursors are the Ru(II) complexes $RuCl_2(PMe_3)_4$ [31, 97] and $RuCl_2(dppe)_2$ [87], although $RuCl_3$ and dppe or PPh_3 can be combined to make an active catalyst [98]. The mechanism, at least for $RuCl_2(PMe_3)_4$, is believed to be hydrogenation of CO_2 to formic acid by the usual insertion mechanism followed by uncatalyzed thermal condensation between the formic acid and the dimethylamine (Eq. (13)). The formic acid/formate salt intermediate is observed spectroscopically [31, 97]. Fortunately, the condensation step seems to be essentially irreversible.

$$CO_2 + H_2 + NHR_2 \underset{\text{catalyst}}{\rightleftharpoons} [NH_2R_2][O_2CH] \xrightarrow{} HC(O)NR_2 + H_2O \tag{13}$$
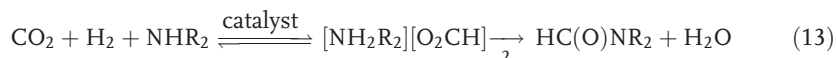
Three alternative mechanisms have been mentioned in the literature. Reduction of CO_2 to CO followed by carbonylation of dimethylamine was ruled out by Haynes et al. [3] for $RhCl(PPh_3)_3$ because no carbonyl complexes were detected. Aminolysis of formate complexes (Eq. (14)) was proposed by Kudo et al. [69], but strong evidence has not been obtained. Finally, CO_2 is known to react with the amine to produce a carbamate salt (Eq. (15)), and it is possible that the pathway to the formamide is by hydrogenation of the carbamate rather than of the CO_2.

$$MO_2CH + NHR_2 \rightarrow MOH + HC(O)NR_2 \tag{14}$$

$$CO_2 + 2NHR_2 \rightleftharpoons [NH_2R_2][O_2CNR_2] \tag{15}$$

For longer-chain or more bulky amines, yields and conversions are often significantly lower, possibly because the carbamate formed (Eq. (15)) is solid [99], but some successful syntheses have been reported. Süss-Fink et al. were able to prepare the formamides of piperidine and pyrrolidine at $140\,°C$ using

Table 17.3 Homogeneous catalyst precursors for the hydrogenation of CO_2, in the presence of dimethylamine, to dimethylformamide.

Catalyst precursor	$P_{H2, CO2}$[a] [atm]	Temperature [°C]	Time [h]	TON	TOF[b] [h^{-1}]	Yield[c] [%]	Reference(s)
Ruthenium							
$RuCl_3$/dppe/$AlEt_3$	29, 29	130	6	3400	570	73	105
$RuCl_2(PPh_3)_3$	29, 29	130	6	2650	440	51	105
$RuCl_2(PMe_3)_4$	80, 130	100	70	420000	6000	71	31, 97
$RuCl_2(PMe_3)_4$	80, 130	100	19	62000	3000	99	31, 97
$RuCl_2(dppe)_2$	85, 130	100	2	740000	360000	18	87
$RuCl_2PH(CH_2OH)_{22}P(CH_2OH)_{32}$	85, 133	100	48	10000	210	100	106
Rhodium							
$RhCl(PPh_3)_3$	28, 28	100	17	43	2.5	11	3
$RhCl(PPh_3)_3$	80, 40	150	5	36	7	65	107
Palladium							
$Pd(CO_3)(PPh_3)_2$	28, 28	100	17	120	7	60	3
$PdCl_2$/$KHCO_3$	80, 40	170	1.5	34	23	99	69
Other metals							
$CdCl_2(PPh_3)_2$	28, 28	125	17	10.5	0.6	4	4
$Pt(CO_3)(PPh_3)_2$	28, 28	100	17	104	6	47	3
$Pt_2(dppm)_3$	67–94, 10–12	75	24	1460	61	na	96
$Pt_2(dppm)_3$	114 total	100	24	1375	57	na	108
$IrCl(CO)(PPh_3)_2$[d]	50–68, 13–17	125	240	1145	5	na	109

a) In some cases, the pressure of CO_2 was not given and was calculated from the total stated pressure minus the pressure of H_2.
b) The TOF values are not directly comparable to each other because some are at complete conversion and some are at partial conversion. They can, however, give an order of magnitude indication. Initial TOF values will be even higher.
c) Data in this column may be either isolated yield or % conversion, depending on data available.
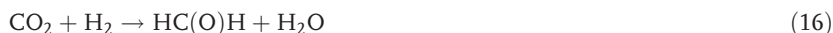d) Using NH_3 to produce formamide.
na = data not available.

Na[Ru$_3$H(CO)$_{11}$] catalyst precursor [100]. Tumas' group [101] obtained 100% conversion to di(*n*-propyl)formamide from di(*n*-propyl)amine by performing the reaction in an ionic liquid at 80 °C. Jessop's group [102] found that adding C$_6$F$_5$OH to the RuCl$_2$(PMe$_3$)$_4$ catalyst precursor allows one to obtain 96–100% conversion to a variety of bulky formamides, including those from heptylamine, piperidine, and benzylamine, at 100 °C (3 µmol Ru, 100 µmol C$_6$F$_5$OH, 5 mmol amine). For less basic amines such as aniline [103], no formamide is obtained unless an additional base is added such as DBU instead of, and not in addition to, the C$_6$F$_5$OH. Baiker's group [99, 104] used RuCl$_2$(dppe)$_2$ catalyst precursor and water as a promoter to prepare a range of formamides from aliphatic amines in very high TON at 100 °C.

17.6
Reduction to Other Products

Reduction of CO$_2$ past formic acid generates formaldehyde, methanol or methane (Eqs. (16–18)), and ethanol can be produced by homologation of the methanol. The liberation of water makes these reactions thermodynamically favorable but economically less favorable. The reductions typically require much higher temperatures than does the reduction to formic acid, and consequently few homogeneous catalysts are both kinetically capable and able to withstand the operating conditions.

$$CO_2 + H_2 \rightarrow HC(O)H + H_2O \tag{16}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{17}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{18}$$

The hydrogenation of CO$_2$ to CO is the reverse water-gas shift reaction, which has been reviewed elsewhere [110, 111].

Hydrogenation to both formaldehyde and formic acid is catalyzed by K[RuCl(EDTA-H)] [21, 112, 113], but the proposed mechanism involved a highly unlikely reverse insertion of CO$_2$ (Eq. (19)).

$$MH + CO_2 \rightarrow MCO_2H \tag{19}$$

Methane production by CO$_2$ hydrogenation has been catalyzed by [PdCl(dppm)]$_2$ (1.5 TON at 120 °C) [78, 89] and Ru$_3$(CO)$_{12}$/I$_2$ (76 TON at 240 °C) [72, 73, 114]. The inclusion of KI in the latter system shifted the selectivity over to methanol production (95 TON) by preventing deposition of Ru metal which would have catalyzed methane production. The mechanism was believed [114] to be reduction of CO$_2$ to CO followed by hydrogenation of the CO to CH$_3$OH via Dombek's [115] mechanism.

Ethanol production by homologation of methanol can be achieved by hydrogenation of CO$_2$ (Eq. (20)) [116]. Sasaki's group showed that both Ru and Co car-

bonyl catalysts are required, as is an iodide salt; in the absence of iodide, methyl formate is obtained. The high-boiling solvent 1,3-dimethyl-2-imidazolidinone (DMI) was required for the reaction, which was typically performed at 180 °C. In a separate study [71], the same group showed that hydrogenation of CO_2 to methanol by these same catalysts also produces ethanol (up to TON 17, TOF $1\,h^{-1}$) because of the *in-situ* homologation of the methanol product.

$$CH_3OH + CO_2 + 3H_2 \xrightarrow[\text{LiI, DMI}]{\overset{Ru_3(CO)_{12}}{Co_2(CO)_8}} CH_3CH_2OH + 2H_2O \tag{20}$$
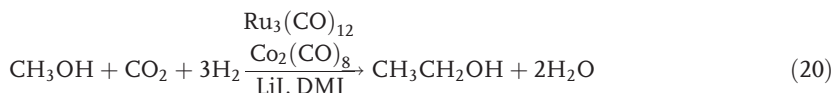
Carboxylic acids have been prepared by CO_2 hydrogenation in the presence of alkyl iodides and catalyzed by the $Ru_3(CO)_{12}/Co_2(CO)_8$ combination (Eq. (21)). Although the yield was not high (2.5 TON, mol acetic acid per mol Co), the reaction is an interesting variation [117].

$$CH_3I + CO_2 + H_2 \xrightarrow[\text{150 pC}]{\overset{Ru_3(CO)_{12}}{Co_2(CO)_8}} CH_3CO_2H + HI \tag{21}$$
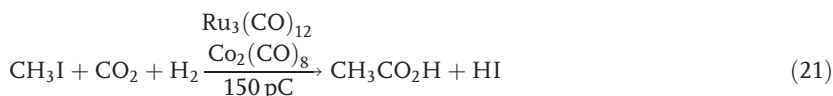
17.7
Concluding Remarks

Highly efficient catalysts have been developed for the hydrogenation of CO_2 to formic acid and formamides, to the point where industrialization could be considered. Researchers have been far less successful in developing efficient homogeneous catalysts and optimum conditions for the hydrogenation of CO_2 to alkyl formates, methanol, methane, and especially oxalic acid. These are the areas in which research efforts are most needed.

Great progress has been made in the understanding of the insertion mechanism of CO_2 hydrogenation to formic acid. However, the evidence for other mechanisms remains circumstantial. Strong evidence for exciting new mechanisms, such as concerted ionic hydrogenation, is unavailable. Because research in this area has progressed far more rapidly during the past decade than in earlier decades, one can anticipate many more new results in the near future and look forward to a greater clarification on the subject of mechanism.

Acknowledgments

Abbreviations

Cl_2bpy	6,6′-dichloro-2,2′-bipyridine
COD	1,5-cyclooctadiene
CYPO	$Cy_2PCH_2CH_2OCH_3$
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dcpb	1,4-bis(dicyclohexylphosphino)butane
dcpe	1,2-bis(dicyclohexylphosphino)ethane
DFT	density functional theory
DHphen	4,7-dihydroxy-1,10-phenanthroline
dippe	1,2-bis(diisopropylphosphino)ethane
DMF	dimethylformamide
DMI	1,3-dimethyl-2-imidazolidinone
DMSO	dimethylsulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppm	1,1-bis(diphenylphosphino)methane
EDTA-H	protonated ethylenediaminetetraacetic acid
hfacac	1,1,1,5,5,5-hexafluoroacetylacetonate
NBD	norbornadiene
PTA	1,3,5-triaza-7-phosphaadamantane
$scCO_2$	supercritical CO_2
TED	triethylenediamine
THF	tetrahydrofuran
TOF	turnover frequency (TON per h)
TON	turnover number (mol product per mol catalyst)
Tp	tris(pyrazolyl)borate
TPPMS	sodium triphenylphosphine monosulfonate
TPPTS	sodium triphenylphosphine trisulfonate
WGSR	water-gas shift reaction

References

1 J. Haggin, *Chem. Eng. News* **1994**, 29.
2 H. Goehna, P. Koenig, *ChemTech* **1994**, 36.
3 P. Haynes, L. H. Slaugh, J. F. Kohnle, *Tetrahedron Lett.* **1970**, 365.
4 P. Haynes, J. F. Kohnle, L. H. Slaugh, U.S. Patent 3 530 182, **1970**.
5 K. Kudo, N. Sugita, Y. Takezaki, *Nihon Kagaku Kaishi* **1977**, 302.
6 P. Munshi, A. D. Main, J. Linehan, C. C. Tai, P. G. Jessop, *J. Am. Chem. Soc.* **2002**, *124*, 7963.

7 B. P. Sullivan, K. Krist, H. E. Guard (Eds.), *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide.* Elsevier, Amsterdam, **1993**.
8 A. Miedaner, C. J. Curtis, R. M. Barkley, D. L. DuBois, *Inorg. Chem.* **1994**, *33*, 5482.
9 I. Bhugun, D. Lexa, J.-M. Savéant, *J. Am. Chem. Soc.* **1994**, *116*, 5015.
10 I. Bhugun, D. Lexa, J.-M. Savéant, *J. Am. Chem. Soc.* **1996**, *118*, 1769.

11 H. Hayashi, S. Ogo, T. Abura, S. Fuku-zumi, *J. Am. Chem. Soc.* **2003**, *125*, 14266.

12 P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259.

13 W. Leitner, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207.

14 P. G. Jessop, F. Joo, C.-C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425.

15 E. B. Reid. In: *McGraw-Hill Encyclopedia of Science and Technology*, Volume 5. McGraw-Hill Book Co., New York, **1982**, p. 670.

16 W. Reutemann, H. Kieczka. In: B. Elvers, S. Hawkins, M. Ravenscroft, J. F. Rounsaville, G. Schulz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, Volume A12, 5th edn. VCH, Weinheim, **1989**, p. 13.

17 B. Jezowska-Trzebiatowska, P. Sobota, *J. Organomet. Chem.* **1974**, *80*, C27.

18 Y. Inoue, H. Izumida, Y. Sasaki, H. Hashimoto, *Chem. Lett.* **1976**, 863.

19 J.-C. Tsai, K. M. Nicholas, *J. Am. Chem. Soc.* **1992**, *114*, 5117.

20 W. Leitner, E. Dinjus, F. Gaßner, *J. Organomet. Chem.* **1994**, *475*, 257.

21 M. M. T. Khan, S. B. Halligudi, S. Shukla, *J. Mol. Catal.* **1989**, *57*, 47.

22 F. Gassner, W. Leitner, *J. Chem. Soc., Chem. Commun.* **1993**, 1465.

23 D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert, C. L. Liotta, *J. Org. Chem.* **2005**, *70*, 5335.

24 D. J. Drury, J. E. Hamlin, European Patent Application 0 095 321, **1983**.

25 E. Graf, W. Leitner, *J. Chem. Soc., Chem. Commun.* **1992**, 623.

26 M. Sakamoto, I. Shimizu, A. Yamamoto, *Organometallics* **1994**, *13*, 407.

27 J. J. Anderson, J. E. Hamlin, European Patent Appl. 0 126 524, **1984**.

28 J. J. Anderson, D. J. Drury, J. E. Hamlin, A. G. Kent, European Patent Application 0 181 078, **1985**.

29 E. A. Karakhanov, S. V. Egazar'yants, S. V. Kardashev, A. L. Maksimov, S. S. Minos'-yants, A. D. Sedykh, *Petroleum Chem.* **2001**, *41*, 268.

30 P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **1994**, *368*, 231.

31 P. G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 344.

32 F. Kohler, H. Atrops, H. Kalali, E. Liebermann, E. Wilhelm, F. Ratkovics, T. Salamon, *J. Phys. Chem.* **1981**, *85*, 2520.

33 K. Wagner, *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 50.

34 F. Kohler, R. Gopal, G. Goetze, H. Atrops, M. A. Demeriz, E. Liebermann, E. Wilhelm, F. Ratkovics, B. Palagyi, *J. Phys. Chem.* **1981**, *85*, 2524.

35 T. Ikariya, P. G. Jessop, R. Noyori, Japan Tokkai 5-274721, **1993**.

36 C. A. Thomas, R. J. Bonilla, Y. Huang, P. G. Jessop, *Can. J. Chem.* **2001**, *79*, 719.

37 N. N. Ezhova, N. V. Kolesnichenko, A. V. Bulygin, E. V. Slivinskii, S. Han, *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 2165.

38 The TOF data from the table were corrected to 20 °C by assuming that every 10° rise doubled the rate. The TOF data were corrected to 1 atm each of H_2 and CO_2 by assuming that the rates were first order with respect to both H_2 and CO_2, but switched to 0 order above 80 atm due to saturation kinetics. The same sequence was obtained if saturation kinetics were not assumed.

39 Y. Musashi, S. Sakaki, *J. Am. Chem. Soc.* **2002**, *124*, 7588.

40 Y. Gao, J. K. Kuncheria, H. A. Jenkins, R. J. Puddephatt, G. P. A. Yap, *J. Chem. Soc., Dalton Trans.* **2000**, 3212.

41 J. Z. Zhang, Z. Li, H. Wang, C. Y. Wang, *J. Mol. Catal. A: Chem.* **1996**, *112*, 9.

42 T. Yamaji, Japan Kokai Tokkyo Koho 140 948, **1981**.

43 C. Yin, Z. Xu, S.-Y. Yang, S. M. Ng, K. Y. Wong, Z. Lin, C. P. Lau, *Organometallics* **2001**, *20*, 1216.

44 S. M. Ng, C. Yin, C. H. Yeung, T. C. Chan, C. P. Lau, *Eur. J. Inorg. Chem.* **2004**, 1788.

45 C. P. Lau, Y. Z. Chen, *J. Mol. Catal. A: Chem.* **1995**, *101*, 33.

46 H. S. Chu, C. P. Lau, K. Y. Wong, *Organometallics* **1998**, *17*, 2768.

47 J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó, *Appl. Catal. A: General* **2003**, *255*, 59.

48 Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga. In: *50th Symposium on Organometallic Chemistry*, Osaka, Japan, **2003**.

49 M. L. Man, Z. Zhou, S. M. Ng, C. P. Lau, *J. Chem. Soc., Dalton Trans.* **2003**, 3727.

50 T. Burgemeister, F. Kastner, W. Leitner, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 739.

51 T. Yamaji, Teijin Ltd., Japan Kokai Tokkyo Koho, 166.146, **1981**.

52 W. Leitner, E. Dinjus, F. Gassner. In: B. Cornils, W.A. Herrmann (Eds.), *Aqueous-Phase Organometallic Catalysis*. Wiley-VCH, Weinheim, **1998**, p. 486.

53 E. Lindner, B. Keppeler, P. Wegner, *Inorg. Chim. Acta* **1997**, *258*, 97.

54 R. Fornika, H. Görls, B. Seemann, W. Leitner, *J. Chem. Soc., Chem. Commun.* **1995**, 1479.

55 H. Hashimoto, S. Inoue, Japanese Patent 07.612, **1978**.

56 C.C. Tai, T. Chang, B. Roller, P.G. Jessop, *Inorg. Chem.* **2003**, *42*, 7340.

57 T. Ito, A. Yamamoto. In: S. Inoue, N. Yamazaki (Eds.), *Organic and Bioorganic Chemistry of Carbon Dioxide*. Kodansha Ltd., Tokyo, **1982**, p. 79.

58 A. Behr. In: W. Keim (Ed.), *Catalysis in C1 Chemistry*. D. Reidel Publishing Co., Dordrecht, **1983**, p. 169.

59 Y. Musashi, S. Sakaki, *J. Am. Chem. Soc.* **2000**, *122*, 3867.

60 C. Bo, A. Dedieu, *Inorg. Chem.* **1989**, *28*, 304.

61 S. Sakaki, K. Ohkubo, *Inorg. Chem.* **1989**, *28*, 2583.

62 T. Matsubara, K. Hirao, *Organometallics* **2001**, *20*, 5759.

63 T. Matsubara, *Organometallics* **2001**, *20*, 19.

64 D.J. Darensbourg, C. Ovalles, *J. Am. Chem. Soc.* **1984**, *106*, 3750.

65 F. Hutschka, A. Dedieu, W. Leitner, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742.

66 F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, *J. Am. Chem. Soc.* **1997**, *119*, 4432.

67 D.N. Kursanov, Z.N. Parnes, M.I. Kalinkin, N. Loim, *Ionic Hydrogenation and Related Reactions*, Harwood Academic Publishers, New York, **1985**.

68 C.S. Pomelli, J. Tomasi, M. Sola, *Organometallics* **1998**, *17*, 3164.

69 K. Kudo, H. Phala, N. Sugita, Y. Takezaki, *Chem. Lett.* **1977**, 1495.

70 G. Laurenczy, F. Joó, L. Nádasdi, *Inorg. Chem.* **2000**, *39*, 5083.

71 K.-I. Tominaga, Y. Sasaki, M. Saito, K. Hagihara, T. Watanabe, *J. Mol. Catal.* **1994**, *89*, 51.

72 K. Tominaga, Y. Sasaki, M. Kawai, T. Watanabe, M. Saito, *J. Chem. Soc., Chem. Commun.* **1993**, 629.

73 K. Tominaga, Y. Sasaki, K. Hagihara, T. Watanabe, M. Saito, *Chem. Lett.* **1994**, 1391.

74 D.J. Darensbourg, C. Ovalles, M. Pala, *J. Am. Chem. Soc.* **1983**, *105*, 5937.

75 L. Skarlos, U.S. Patent 3 720 591, **1973**.

76 F.R. Keene, B.P. Sullivan. In: B.P. Sullivan (Ed.), *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*. Elsevier, Amsterdam, **1993**, p. 118.

77 M.M. Ali, H. Sato, T. Mizukawa, K. Tsuge, M. Haga, K. Tanaka, *Chem. Commun.* **1998**, 249.

78 B. Denise, R.P.A. Sneeden, *J. Organomet. Chem.* **1981**, *221*, 111.

79 C.-C. Tai, P. G. Jessop, unpublished material, **2002**.

80 H. Phala, K. Kudo, S. Mori, N. Sugita, *Bull. Inst. Chem. Res., Kyoto Univ.* **1985**, *63*, 63.

81 Y. Inoue, Y. Sasaki, H. Hashimoto, *J. Chem. Soc., Chem. Commun.* **1975**, 718.

82 P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Chem. Soc., Chem. Commun.* **1995**, 707.

83 P.G. Lodge, D.J.H. Smith, European Patent Application 0 094 785, **1983**.

84 G.O. Evans, C.J. Newell, *Inorg. Chim. Acta* **1978**, *31*, L387.

85 D.J. Darensbourg, C. Ovalles, *CHEMTECH* **1985**, *15*, 636.

86 I.S. Kolomnikov, T.S. Lobeeva, M.E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 2329.

87 O. Kröcher, R.A. Köppel, A. Baiker, *Chem. Commun.* **1997**, 453.

88 H. Hashimoto, S. Inoue, Japanese Patent 138 614, **1976**.

89 B. Denise, R.P.A. Sneeden, *CHEMTECH* **1982**, February, 108.

90 B. Beguin, B. Denise, R.P.A. Sneeden, *J. Organomet. Chem.* **1981**, *208*, C18.

91 B.F. Hoskins, R.J. Steen, T.W. Turney, *Inorg. Chim. Acta* **1983**, *77*, L69.

92 D.J. Darensbourg, C. Ovalles, *J. Am. Chem. Soc.* **1987**, *109*, 3330.

93 H. Koinuma, H. Kato, H. Hirai, *Chem. Lett.* **1977**, 517.

94 K.-I. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, *J. Chem. Soc., Chem. Commun.* **1995**, 1489.

95 H. Bipp, H. Kieczka. In: B. Elvers, S. Hawkins, M. Ravenscroft, J.F. Rounsaville, G. Schulz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, Volume A12, 5th edn. VCH, Weinheim, **1989**, p. 1.

96 S. Schreiner, J.Y. Yu, L. Vaska, *Inorg. Chim. Acta* **1988**, *147*, 139.

97 P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1994**, *116*, 8851.

98 M. Rohr, J.-D. Grunwaldt, A. Baiker, *J. Mol. Catal. A: Chem.* **2005**, *226*, 253.

99 L. Schmid, M.S. Schneider, D. Engel, A. Baiker, *Catal. Lett.* **2003**, *88*, 105.

100 G. Süss-Fink, M. Langenbahn, T. Jenke, *J. Organomet. Chem.* **1989**, *368*, 103.

101 F.C. Liu, M.B. Abrams, R.T. Baker, W. Tumas, *Chem. Commun.* **2001**, 433.

102 P. Munshi, P.G. Jessop, E. McKoon, unpublished material, **2002**.

103 P. Munshi, D. Heldebrant, E. McKoon, P.A. Kelly, C.-C. Tai, P.G. Jessop, *Tetrahedron Lett.* **2003**, *44*, 2725.

104 L. Schmid, A. Canonica, A. Baiker, *Applied Catalysis A: General* **2003**, *255*, 23.

105 Y. Kiso, K. Saeki, Vol. 22 March, Japan Kokai 36617, **1977**, p. 9.

106 Y. Kayaki, T. Suzuki, T. Ikariya, *Chem. Lett.* **2001**, 1016.

107 H. Phala, K. Kudo, N. Sugita, *Bull. Inst. Chem. Res., Kyoto Univ.* **1981**, *59*, 88.

108 S. Schreiner, J.Y. Yu, L. Vaska, *J. Chem. Soc., Chem. Commun.* **1988**, 602.

109 L. Vaska, S. Schreiner, R.A. Felty, J.Y. Yu, *J. Mol. Catal.* **1989**, *52*, L11.

110 P. Ford. In: B.P. Sullivan, K. Krist, H.E. Guard (Eds.), *Electrochemical and electrocatalytic reactions of carbon dioxide.* Elsevier, Amsterdam, **1993**, Chapter 3.

111 M. Torrent, M. Sola, G. Frenking, *Chem. Rev.* **2000**, *100*, 439.

112 M.M.T. Khan, S.B. Halligudi, S. Shukla, *J. Mol. Catal.* **1989**, *53*, 305.

113 M.M.T. Khan, S.B. Halligudi, N.N. Rao, S. Shukla, *J. Mol. Catal.* **1989**, *51*, 161.

114 K. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2837.

115 B.D. Dombek, *J. Organometal. Chem.* **1983**, *250*, 467.

116 K.-I. Tominaga, Y. Sasaki, T. Watanabe, M. Saito. In: T. Inui, M. Anpo, K. Izui, S. Yanagida, T. Yamaguchi (Eds.), *Advances in Chemical Conversions for Mitigating Carbon Dioxide.* Elsevier, Amsterdam, **1998**, p. 495.

117 A. Fukuoka, N. Gotoh, N. Kobayashi, M. Hirano, S. Komiya, *Chem. Lett.* **1995**, 567.