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Homogeneous Hydrogenation of Carbon Dioxide

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I. Introduction

Carbon dioxide (CO_2) is of the greatest interest as a C_1 feedstock because of the vast amounts of carbon which exist in this form and because of the low cost of bulk CO_2. Currently, toxic carbon monoxide, the main competitor for many processes, is used in industry instead because CO_2 is perceived to be less reactive and its efficient catalytic conversion has remained elusive. Because CO_2 is a highly oxidized, thermodynamically stable compound, its utilization requires reaction with certain high energy substances or electroreductive processes. Catalytic hydrogenation is one of the most promising approaches to CO_2 fixation. Recent research has shown that high catalytic efficiency, yields, and rates of reaction can be obtained from CO_2 with optimum conditions and catalysts.

The value of the products from CO_2 fixation is not the only consideration prompting research in this area. Any removal of CO_2 from industrial emissions in order to reduce the greenhouse effect would put large amounts of CO_2 on the market. Recycling rather than storage of CO_2 is more attractive if economical processes are available for conversion to useful bulk products.[1]

This review will describe the simplest and most studied reactions of CO_2: the catalytic reactions with H_2 in the presence or absence of other reactive species. The mechanisms of homogeneously catalyzed reactions will be emphasized. Subjects which will not be covered, aside from brief mentions, include stoichiometric reactions of CO_2 with complexes (see below), the reverse water gas shift reaction,[2] hydrosilylation,[3-5] and electrochemical or photochemical reductions[6-9] of CO_2. C–C bond forming reactions of CO_2 were described in an earlier *Chemical Reviews* article.[10] Some reviews of stoichiometric reactions of CO_2 have also mentioned catalytic reactions, but recent comprehensive reviews of CO_2 hydrogenation are unavailable.

The hydrogenation of CO_2 is paradoxical, as Eisenberg discussed in an earlier review.[11] In order to reduce CO_2 beyond the level of formic acid, an oxygen sink is required. In the hydrogenation of CO_2 to formaldehyde, CO, methanol, or methane, water acts as the sink, but the hydrogen which is thus consumed was prepared by the water gas shift reaction (WGSR) in which CO_2 is the oxygen sink. In this way, CO_2 acts as its own oxygen sink. This is a problem for

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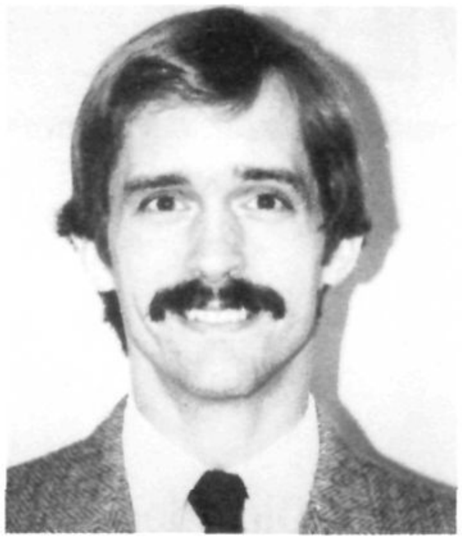


Philip G. Jessop received his B.Sc. from the University of Waterloo in 1986. Research into the kinetics of reactions of hydrido and thiolato ruthenium complexes, under the supervision of Professor Brian R. James of the University of British Columbia, led to the award of a Ph.D. in 1991. During a postdoctoral appointment with Professor Robert H. Morris at the University of Toronto, he studied molecular hydrogen complexes, ligand acidity, and, in a separate project, the properties of deuterated polymers. At ERATO with Professor R. Noyori, he is investigating the use of supercritical carbon dioxide as a reaction medium for homogeneous catalysis.

Takao Ikariya was born in Matsumoto, Japan, in 1948 and now is a research manager of the ERATO Molecular Catalysis Project of JRDC (Research Development Corporation of Japan) which is directed by Professor Ryoji Noyori. After he received his Ph.D. in 1976 from the Tokyo Institute of Technology under the direction of Professor Akio Yamamoto, he was appointed assistant professor in the Department of Synthetic Chemistry at the University of Tokyo. He worked on asymmetric reactions catalyzed by chiral ruthenium complexes, with Professor Sadao Yoshikawa. He spent one and a half years in 1979–1981 as the postdoctoral fellow in Professor Robert H. Grubbs' group at Caltech. In 1985 he moved to the central research center of NKK Corp. where he developed a carbonylation reaction of nitrobenzene. In 1991 he moved to the ERATO project and is currently interested in stereocontrolled living polymerization of acetylenes and homogeneous catalysis in supercritical carbon dioxide.

Ryoji Noyori, born in Kobe in 1938, completed his undergraduate study in 1961 and his Master's degree in 1963 at Kyoto University. He subsequently became Research Associate in the laboratory of Professor Hitosi Nozaki at the same university, receiving his Ph.D. degree in 1967. In the following year, he was appointed Associate Professor in the Department of Chemistry at Nagoya University. He spent a postdoctoral year with Professor E. J. Corey at Harvard University in 1969–1970, and shortly afterward returned to Nagoya, where he was promoted to Professor in 1972. He holds a joint appointment as Professor at Kyushu University and is directing the ERATO Molecular Catalysis Project (1991–1996) of the Research Development Corporation of Japan. His research interests are synthetic organic chemistry, main-group and transition metal organic chemistry, homogeneous catalysis, asymmetric synthesis, and physical organic chemistry. In the ERATO project he is concentrating on polymer synthesis and the use of supercritical fluids as new reaction media, in addition to his interests in asymmetric catalysis.

the supposedly beneficial environmental impact[1] of the use of CO_2 as a carbon source; its reduction, for example to methanol, using H_2 from the WGSR does not result in the net consumption of CO_2, but rather in its net production (eqs 1–3).

$$3CO + 3H_2O \rightarrow 3CO_2 + 3H_2 \qquad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (2)$$

$$3CO + 2H_2O \rightarrow CH_3OH + 2CO_2 \qquad (3)$$

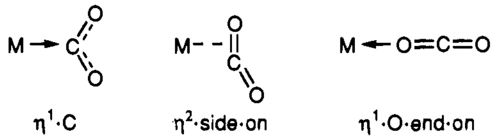
If, in the future, solar or hydrothermally powered electrolysis of water were to become a major method for the production of H_2, then methanol synthesis would result in the overall consumption of CO_2. In areas of the world where transportation costs increase the price of methanol, production of methanol from CO_2 and H_2 is economically feasible despite the cost of H_2. Industrial plants using heterogeneous catalysts for this process have been used or are being planned.[12,13]

The hydrogenation of CO_2 to CO, hydrocarbons, and alcohols is thermodynamically favorable because of the concomitant production of water. However, hydrogenation to formic acid is not thermodynamically favorable. If reasonable yields are to be obtained, the formic acid must be stabilized by addition of a reagent such as a base, giving formate salts, an alcohol, giving formate esters, a nontertiary amine, giving formamides, or an epoxide, giving diol formates. The manner of stabilization of the formic acid is the parameter by which this review has been divided into sections. Formate esters or formamides are often produced via formic acid. It is a mistake, however, to assume that the production of these products by CO_2 hydrogenation necessarily requires formic acid as an intermediate. Although evidence is yet weak, formic acid-independent pathways should be possible. The possibilities will be described.

The stoichiometric reactions of CO_2 with transition metal complexes are important to an understanding of the mechanisms in this review, but they have been reviewed at least 16 times,[7,9,11,12,14–25] so further review, beyond the following brief comments, is considered unnecessary.

Carbon dioxide can bind as a ligand in several geometries, a few of which are shown in Scheme 1. Examples of the η^1 C-bound and η^2 geometries have

Scheme 1. Three Modes of Coordination of CO_2 to Mononuclear Metal Centers



been confirmed by X-ray crystallography.[26-28] In some complexes, the η^1 C-bound structure is stabilized by interaction of the O atoms with electrophilic atoms such as other metals[12,29] or protons of acidic coligands.[30] Only spectroscopic data are available to suggest that the η^1 O-bound geometry occurs in some complexes.[12]

The actual catalytic hydrogenation mechanism may not necessarily involve such metal–CO_2 complexes; free CO_2 molecules could react directly with metal hydrides, for example. The insertion reactions of CO_2 into metal–ligand bonds may require predissociation of an ancillary ligand or a concerted process may occur.[15,22,31-34] Insertion products have two possible geometries; normal insertion forms an η^1 or η^2 O-bonded ligand containing a new C–X bond (eq 4)

$$MX + CO_2 \rightarrow M(O_2CX) \qquad (4)$$
$$X = H, R, OR, NR_2$$

while abnormal insertion forms a C-bonded ligand containing a new O–X bond (eq 5):

$$MX + CO_2 \rightarrow M(CO_2X) \qquad (5)$$
$$X = H, R$$

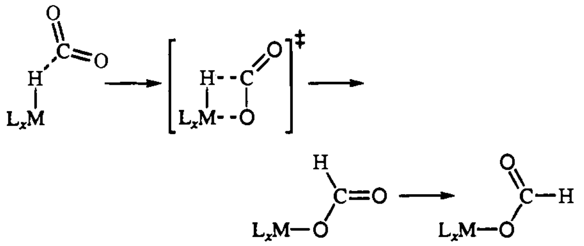
Normal insertion is well established for X = H, R, OR, or NR_2. However, abnormal insertion is not known for X = OR or NR_2 and is rare for X = R.[12] Abnormal insertion into metal hydride bonds has been invoked as a mechanistic step of catalytic cycles but clear examples of the stoichiometric reaction are lacking. The only indirect evidence available for such a reaction was the isolation of a cobalt complex from reaction 6. The structure of the complex is unknown

$$CoH(N_2)[P(C_6H_5)_3]_3 + CO_2 \rightarrow Co(CO_2H)[P(C_6H_5)_3]_3 \qquad (6)$$

$$Co(CO_2H)[P(C_6H_5)_3]_3 \xrightarrow{CH_3I} \xrightarrow[BF_3]{CH_3OH} CH_3CO_2CH_3 \qquad (7)$$

but was assumed by the discoverers to be a hydroxycarbonyl complex because of a subsequent reaction (eq 7).[25,35] Hydroxycarbonyl complexes can be formed by other reactions such as hydroxide attack on a carbonyl ligand. These complexes can decarboxylate,[36] an important step in the WGSR,[2,37-40] which suggests that the reverse reaction, abnormal insertion of CO_2 into an M–H bond, is possible.

The mechanism of normal insertion reactions (eq 4) depends on a number of factors, most important being the nature of X. For insertions into M–H bonds, the following mechanism has been studied by ab initio molecular orbital calculations:[34,41]



(8)

Other mechanisms could involve $M(H)(CO_2)$ intermediates. Reactions of metal hydride complexes with CO_2 in the presence of water, alcohol, or secondary amine may actually be reactions with carbonic acid, carbonic acid monoester, or carbamic acid. The products are carbonate, alkyl carbonate, or carbamate complexes (eq 9):

$$CO_2 + HX \rightarrow HO_2CX \xrightarrow{MH} MO_2CX + H_2 \qquad (9)$$
$$X = OH, OR, NR_2$$

For insertions of CO_2 into metal alkoxide or amide bonds, in addition to simple insertion, a free alcohol- or amine-catalyzed mechanism is available (eq 10):[42-44]

$$CO_2 + HX \rightarrow HO_2CX \xrightarrow{MX} MO_2CX + HX \qquad (10)$$
$$X = OH, OR, NR_2$$

For further description of the stoichiometric reactions of CO_2 with transition metal complexes, refer to the many review articles mentioned above.

The tables in the present review are comprehensive lists of reports of relevant reactions. From each publication, the reaction with the highest catalytic efficiency, turnover number (TON, moles of product per mole of catalyst), was chosen for inclusion in the table. Most of the pressures cited are the pressures at room temperature. Because the reactions are usually carried out at elevated temperatures, the true reaction pressures must be higher. Exceptions are the supercritical studies in which the pressure at reaction temperature is cited. All thermodynamic data were calculated for 25 °C from published data.[45-47] For aqueous systems, data for standard state, unit molality were used.

II. Producing Formic Acid or Formate Salts

Formic acid is currently prepared via sodium formate from the reaction of NaOH with CO under pressure and at 210 °C. Uses of formic acid include dehairing, tanning, preparation of silage, reduction of metallic ions and dyes, and as a precursor for the preparation of esters, allyl alcohol, oxalic acid, and aspartame.[48,49] The synthesis of formic acid/formate anion by the hydrogenation of CO_2 was first discovered by Farlow and Adkins in 1935 using Raney nickel as the catalyst (eq 11).[50] The first homogeneously catalyzed example was reported by Inoue et al. in 1976.[51]

$$H_2 + CO_2 \rightarrow HCO_2H \qquad (11)$$

Table 1. Homogeneous Hydrogenation of CO_2 to Formic Acid

catalyst precursor	solvent	additives	P_{H_2/CO_2} (atm)	T (°C)	t (h)	TON	TOF (h^{-1})	ref
$Pd(dppe)_2$	C_6H_6	$N(C_2H_5)_3 + H_2O$	25/25	110	20	62	3	51
$RuH_2[P(C_6H_5)_3]_4$	C_6H_6	$N(C_2H_5)_3 + H_2O$	25/25	rt	20	87	4	51
$PdCl_2$	H_2O	KOH	110/na	160	3	1580	530	55
$Pd(dppe)_2$	C_6H_6	NaOH	24/24	rt	20	17	0.9	56
$RuH_2[P(C_6H_5)_3]_4$	C_6H_6	Na_2CO_3	25/25	100	4	169	42	58
$RhCl[P(C_6H_5)_3]_3$	C_6H_6	Na_2CO_3	60/55	100	3	173	58	57
$[RuCl_2(CO)_2]_n$	H_2O + *i*-PrOH	$N(C_2H_5)_3$	81/27	80	0.3[a]	400	1300	61
K[RuCl(EDTA·H)]	H_2O	–	3/17	40	0.5	na	250	67
$[Rh(nbd)\{P(CH_3)_2(C_6H_5)\}_3]BF_4$	THF	H_2O	48/48	40	48	128	3	65
$[Rh(cod)Cl]_2$	DMSO	$N(C_2H_5)_3$ + dppb	20/20	rt	22	1150	52	52
$[Rh(cod)Cl]_2$	DMSO	$N(C_2H_5)_3$ + dippe	40 total	24	18	205	11	70
$RhCl[P(C_6H_4\cdot m\cdot SO_3Na)_3]_3$	H_2O	$NH(CH_3)_2$	20/20	rt	12	3439	287	59
$PdCl_2[P(C_6H_5)_3]_2$	C_6H_6	$N(C_2H_5)_3 + H_2O$	50/50	rt	na	15	na	62
$RuH_2[P(CH_3)_3]_4$	$scCO_2$	$N(C_2H_5)_3 + H_2O$	85/120	50	1	1400	1400	60
$RuCl_2[P(CH_3)_3]_4$	$scCO_2$	$N(C_2H_5)_3 + H_2O$	85/120	50	47	7200	150	60
$[RhH(cod)]_4$	DMSO	$N(C_2H_5)_3$ + dppb	40 total	rt	0.8	312	390	53
$[RhH(cod)]_4$	DMSO	$N(C_2H_5)_3$ + dppb	40 total	rt	18	2200	122	53

[a] Reaction time was not stated. Calculated from highest reported rate and conversion.

The homogeneous catalysts which have been found to be effective for this reaction are complexes of the 2nd and 3rd row metals of groups 8 through 10, usually with halides or hydride as anionic ligands and phosphines as neutral ligands. Deposited Rh metal is not active for this reaction,[52,53] but Pd metal is active for a closely related reaction (section VI).[54]

Addition of a base improves the enthalpy of the reaction, while dissolution of the gases improves the entropy (eqs 12–14).

$$CO_2(g) + H_2(g) \rightarrow HCO_2H(l) \qquad (12)$$

$$\Delta G° = 32.9\ \text{kJ/mol}; \Delta H° = -31.2\ \text{kJ/mol}; \Delta S° = -215\ \text{J/(mol K)}$$

$$CO_2(g) + H_2(g) + NH_3(aq) \rightarrow HCO_2^-(aq) + NH_4^+(aq) \qquad (13)$$

$$\Delta G° = -9.5\ \text{kJ/mol}; \Delta H° = -84.3\ \text{kJ/mol}; \Delta S° = -250\ \text{J/(mol K)}$$

$$CO_2(aq) + H_2(aq) + NH_3(aq) \rightarrow HCO_2^-(aq) + NH_4^+(aq) \qquad (14)$$

$$\Delta G° = -35.4\ \text{kJ/mol}; \Delta H° = -59.8\ \text{kJ/mol}; \Delta S° = -81\ \text{J/(mol K)}$$

Systems which do not include base have TONs less than 200, while systems with base have TONs up to 7200 (Table 1). Many systems yield no formic acid whatsoever in the absence of base. Bases used include inorganic bases[51,55–58] and trialkylamines. Dialkylamines can also be used, especially for aqueous systems because of greater solubility,[59] but at higher temperatures dialkylformamides are formed instead of formate salts (section VI). The yield of formic acid can exceed, by up to 80%, the amount of amine used as base.[52,60] Separation of the amine base and the formic acid product is possible by adding another acid[61] to give formic acid and a salt, or by adding another base to give free amine and a formate salt.[52,62] If the new base is a high-boiling amine such as an imidazole, thermal decomposition of the formate salt yields formic acid and free amine, which can be recycled.[63,64]

Unless the hydrogenation catalyst is removed, the formic acid decomposes to CO_2 and H_2 once the pressures of these gases are reduced,[52,53] because catalysts for reaction 11 are also catalysts for the reverse reaction.[65,66] Decomposition to CO and H_2O is also possible.[67] Formic acid is thus a possible intermediate in the WGSR[37,68,69] and its reverse.

In comparison with systems in organic solvents, those in aqueous solution have had high rates[61,67] and yields.[59] The reasons for this have not yet been identified. Among organic solvents, polar aprotic solvents increase the entropy of the formic acid product, thereby allowing greater yields.[53] The extremely high miscibility of H_2 in supercritical CO_2 ($scCO_2$) is believed to be the reason for the very high rates observed in that medium (see section VIII).[60,71,72]

An accelerating effect of small amounts of added water in organic solvents[51,65] is consistent with a number of mechanisms and therefore cannot be considered evidence for any in particular. It is also possible that a donative interaction between water and the carbon atom of CO_2 increases the nucleophilicity of the CO_2 oxygen atoms and thus increases its ability to bind to the metal center. Water and CO_2 interacting in such a way have been calculated by ab initio methods to be more stable than the two species apart.[73] A similar interaction between amine and CO_2 could in theory assist the reaction in the presence of amines, but ab initio calculations suggest that the increase in reactivity would be small.[74]

A. Via Carbon Monoxide

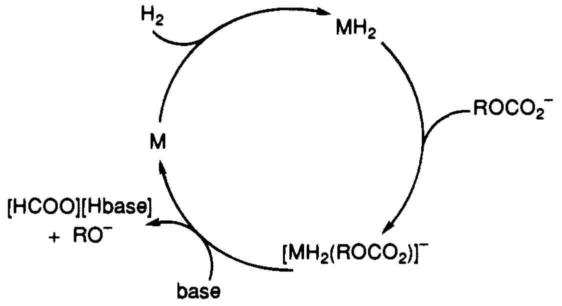
A possible mechanism for reaction 11 is the production of CO and water by the reverse WGSR, followed by the production of formic acid from these two compounds (eq 15):

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \rightleftharpoons HCO_2H \qquad (15)$$

The second step can proceed via hydroxide attack on CO coordinated to a metal.[2]

Scheme 2. The Carbonate Mechanism for the Hydrogenation of CO_2 in the Presence of (a) $PdCl_2$ and KOH (R = H)[54,55] or (b) $RhCl[P(C_6H_5)_3]_3$, CH_3OH, and TED (R = CH_3)[76]

$$RO^- + CO_2 \rightleftharpoons ROCO_2^-$$



This mechanism for reaction 11 can be ruled out experimentally by the addition of CO gas to the reaction mixture, which would probably poison most of the catalysts in Table 1. This has been done for a few systems.[51,65]

B. Via Carbonate

Some Rh hydrides do not react with CO_2 to give formates by insertion but rather give carbonates with incorporation of water.[75] Hydrogenolysis of carbonate ligands theoretically could lead directly to formic acid, but we are unaware of any concrete examples of this transformation.[23] The hydrogenation of carbonate and bicarbonate salts to formate salts catalyzed by Pd complexes has been reported,[51,55] although the intermediacy of CO_2 cannot yet be discounted.

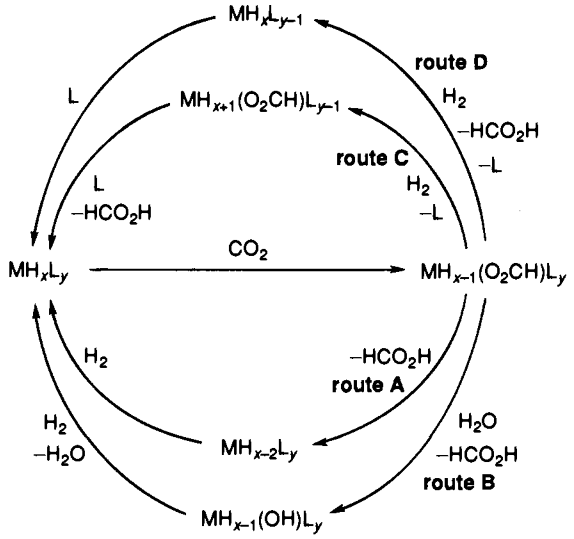
This mechanism was proposed by Kudo et al. for the KOH/$PdCl_2$ system (Scheme 2).[54,55] The derived rate law for this mechanism was consistent with the observed kinetic data.

This mechanism could also operate with amines as bases in the presence of a catalytic amount of water, although one wonders whether this mechanism, if proven to exist, would be more prevalent among aqueous or alcoholic systems.

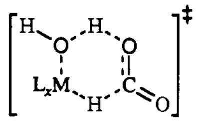
C. Via Normal CO_2 Insertion into an M−H Bond

Transition metal phosphine chlorido complexes are converted to hydride complexes in the presence of base and hydrogen gas.[77] Normal CO_2 insertion into the metal hydride bond generates a metal formate complex. The subsequent liberation of formic acid and the replenishment of the hydride ligand can occur by at least four routes, which are summarized in Scheme 3.

Scheme 3. Mechanisms of Catalytic Hydrogenation of CO_2 to Formic Acid via CO_2 Insertion into an M−H Bond



(a) In route A, reductive elimination of formic acid leads to the reduced intermediate $MH_{x-2}L_y$. For the case of $MH_2(PR_3)_4$ catalysts (M = Fe, Ru, Os), for example, this would correspond to the M(0) complexes $M(PR_3)_4$, which may be susceptible to carbonate or carbonyl formation.[78] In the absence of such deactivation, the hydride ligands can be replenished by oxidative addition of H_2. Such a mechanism was proposed by Tsai and Nicholas[65] for the catalyst precursor $[Rh(nbd)\{P(CH_3)_2(C_6H_5)\}_3]BF_4$ on the basis of the detection of the intermediate complexes $[H_2Rh\{P(CH_3)_2(C_6H_5)\}_3L]^+$ (L = H_2O, THF) and $[HRh(\eta^2\text{-}O_2CH)\{P(CH_3)_2(C_6H_5)\}_2(\text{solvent})]^+$ by stoichiometric reactions with H_2 and CO_2, respectively, monitored by high-pressure IR spectroscopy. The same authors speculated that water, as an ancillary ligand on the catalyst, could accelerate the CO_2 insertion step of this mechanism by hydrogen bonding to one of the oxygen atoms of the incoming CO_2 molecule.

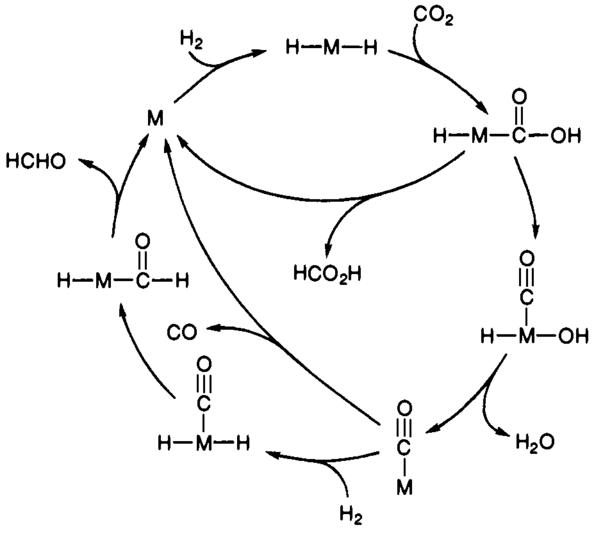


(b) Route B, the hydrolysis of the metal formate complex, yields a hydroxide complex. This was proposed by Inoue et al. to account for the requirement of a catalytic amount of water in the system $Pd(dppe)_2$.[51] If the hydrolysis is the rate-determining step, then increased amounts of water should presumably increase the rate, until the rate of the hydrolysis step is no longer rate limiting. Inoue et al. observed increasing rates at increasing concentrations of water up to 1 mol of water per mole of catalyst.[51] This route was also proposed by Koinuma et al.[79] for the carbonylation of $RhCl[P(C_6H_5)_3]_3$ by CO_2 and H_2 via formic acid.

(c) Route C, the addition of H_2 to the formate complex, may require prior dissociation of a ligand. Route C was proposed for the production of methyl formate via formic acid catalyzed by $M(O_2CH)(CO)_5^-$ (M = W, Cr),[80] because the analogous acetate complex reacts with H_2 and CH_3OH to generate $CH_3CO_2CH_3$, but does not react with CH_3OH in the absence of H_2. Dissociation of a CO ligand is believed to be required before H_2 coordination, because CO dissociation is facile and CO pressure inhibited the reaction.

(d) Route D, direct hydrogenolysis of the M−O bond without prior oxidative addition of H_2 to the metal, is also possible, either by a concerted hydrogenolysis or via a nonclassical intermediate[81] $MH_{x-1}(\eta^2\text{-}H_2)(O_2CH)L_{y-1}$.

Scheme 4. A Mechanism for the Hydrogenation of CO_2 to Formic Acid, Formaldehyde, and CO[24]



The mechanism of Scheme 3 is analogous to the "dihydride" route for olefin hydrogenation.[82] An analogue of the "unsaturate" route is also possible, in which CO_2 would coordinate before H_2 adds. A variation of this, proposed by Taqui Khan et al.,[67] will be described in the following section.

D. Via Abnormal CO_2 Insertion into an M–H Bond

A mechanism for hydrogenation of CO_2 to formic acid, CO, and formaldehyde based on abnormal CO_2 insertion (Scheme 4) has been suggested.[24]

Taqui Khan et al.,[67] who used K[RuCl(EDTA-H)] as a catalyst, proposed without clear evidence a mechanism involving both formate and hydroxycarbonyl complex intermediates, one reacting with water to produce formic acid and the other reacting with H_2 to produce formaldehyde.

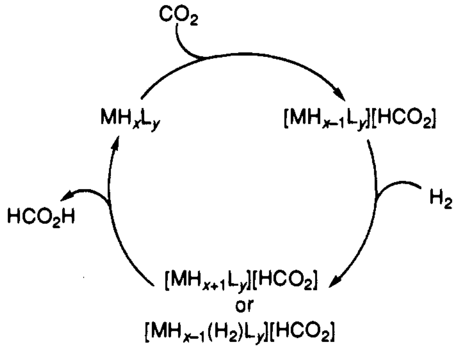
Denise and Sneeden[83] suggested that abnormal CO_2 insertion is a step in the hydrogenation of CO_2 in the presence of alcohols and Pd diphosphine catalysts because they observed dialkyl oxalates as minor products with up to 0.002 TON.

Mechanisms for electrochemical and photochemical CO_2 reductions with hydroxycarbonyl complex (MCO_2H) or metalloformate anion (MCO_2^-) intermediates have been proposed.[8,84,85]

E. Via Hydride Transfer to CO_2

Hydride transfer from a complex to CO_2 (Scheme 5) was proposed by Burgemeister et al.[70] for the reaction catalyzed by $RhH(dppp)_2$, because each of the three intermediates in the cycle was observed by the stepwise stoichiometric reactions. The mechanism of hydride transfer could be either intramolecular, with hydride transfer to a CO_2 ligand followed by formate ion loss, or intermolecular, with hydride transfer from the metal to an unbound CO_2 molecule.[86]

Scheme 5. A Mechanism[70] for the Catalytic Hydrogenation of CO_2 to Formic Acid via Hydride Transfer to CO_2



III. Producing Methanol, Methane, and Carbon Monoxide

The hydrogenation of CO_2 to CO, the reverse WGSR (eq 16), is equivalent to hydrogenation to formic acid followed by dehydration. The homogeneously catalyzed water gas shift reaction has been reviewed sufficiently recently that repetition here is not necessary.[2] The catalysis of CO_2 reduction to formic acid and formaldehyde by K[RuCl(EDTA-H)] was discussed in section II.D. These two products subsequently decomposed to CO and H_2.[67] The homogeneously catalyzed reverse WGSR has been reported by only a few other groups (vide infra). Hydrogenation of CO_2 beyond formic acid, formaldehyde, and CO produces methanol, methane, and occasionally higher alcohols and hydrocarbons. Heterogeneous catalysis of the hydrogenation of CO_2 to CH_3OH and hydrocarbons has been reviewed.[12,23,83] Very few research papers have described the homogeneous catalysis of such reactions. The thermodynamics are neutral or favorable because of the production of water from hydrogen (eqs 16–18), but the economics are unfavorable for the same reason.

$$CO_2(aq) + H_2(aq) \rightarrow CO(aq) + H_2O(l) \quad (16)$$

$$\Delta G^\circ = 11\ \text{kJ/mol};\ \Delta H^\circ = 11\ \text{kJ/mol};\ \Delta S^\circ = -0.8\ \text{J/(mol K)}$$

$$CO_2(aq) + 3H_2(aq) \rightarrow CH_3OH(l) + H_2O(l) \quad (17)$$

$$\Delta G^\circ = -79\ \text{kJ/mol};\ \Delta H^\circ = -106\ \text{kJ/mol};\ \Delta S^\circ = -88\ \text{J/(mol K)}$$

$$CO_2(aq) + 4H_2(aq) \rightarrow CH_4(l) + 2H_2O(l) \quad (18)$$

$$\Delta G^\circ = -193\ \text{kJ/mol};\ \Delta H^\circ = -230\ \text{kJ/mol};\ \Delta S^\circ = -125\ \text{J/(mol K)}$$

Denise and Sneeden[83,87] reported the use of dppm complexes of Pd as homogeneous catalysts for the hydrogenation of CO_2 to CH_4 (up to 1.5 TON), CO (0.2 TON), and other products (Table 2). Tominaga et al.[88,89] reported the use of $Ru_3(CO)_{12}$ with halide salts as catalysts for the conversion of CO_2 to CO, methanol, and methane. The halide salts were required to stabilize the catalyst against reduction to Ru metal which would heterogeneously catalyze hydrogenation to methane. The homogeneous catalyst system catalyzed the reverse WGSR rapidly to CO. Further reaction caused the amount of CO to decrease and methanol increase. Methane and ethane production was slower. An experiment with extra methanol added showed increased yields of CH_4,

Table 2. Homogeneous Hydrogenation of CO_2 to CH_3OH, CH_4, or Other Products

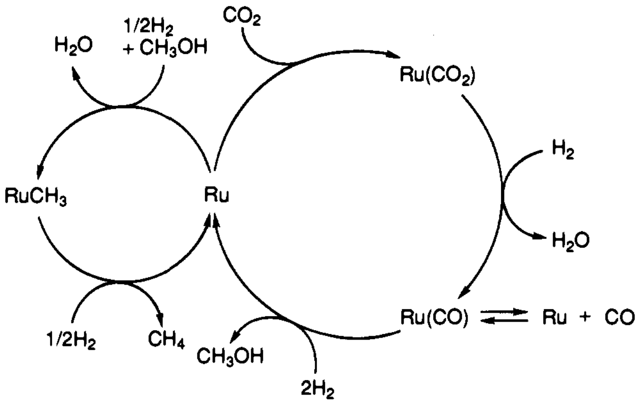
catalyst	solvent	additive	T (°C)	t (h)	CO (TON)	CH_3OH (TON)	CH_4 (TON)	other (TON)	ref(s)
$[PdCl(dppm)]_2$	C_2H_5OH	$N(C_2H_5)_3$	120	24	na	0	1.5	3.8[a]	83,87
Ru_3CO_{12}	NMP	KI	240	3	33	95	24	0.5[b]	88
Ru_3CO_{12}	NMP	I_2	240	3	27	2	76	0.5[b]	88
Ru_3CO_{12}	NMP	ZnI_2	240	3	73	4	4	0	88
Ru_3CO_{12}	NMP	[PPN]Cl	200	5	68	16	5	0	89

[a] $HCO_2C_2H_5$. [b] C_2H_6.

Table 3. Homogeneous Hydrogenation of CO_2 and Alcohols to Alkyl Formates

catalyst precursor	solvent	additives	P_{H_2/CO_2} (atm)	T (°C)	t (h)	TON	TOF (h^{-1})	ref(s)
$HFe_3(CO)_{11}^-$	CH_3OH	–	20/20	175	96	6	0.06	95
$HCO_2W(CO)_5^-$	CH_3OH	–	17/17	125	24	16	0.7	80
$H_3Ru_4(CO)_{12}^-$	CH_3OH	–	17/17	125	24	7	0.3	96
$IrH_3[P(C_6H_5)_3]_3$	C_6H_6	$CH_3OH + BF_3$	30/30	100	na	38	na	94
$Pd(dppe)_2$	CH_3OH	$N(C_2H_5)_3$	25/25	140	21	24	1.1	97
$RhCl[P(C_6H_5)_3]_3$	C_2H_5OH	$N(C_2H_5)_3$	25/25	140	21	30	1.4	97
$Pd(dppm)_2$	C_2H_5OH	$N(C_2H_5)_3$	70/30	160	21	58	2.8	98
$RhCl[P(C_6H_5)_3]_3$	CH_3OH	$NaOCH_3$	68/29	140	21	27	1.3	56
$Pd(dppm)_2$	C_2H_5OH	$N(C_2H_5)_3$	15/15	120	24	9	0.4	83,102
$RuCl_2[P(C_6H_5)_3]_3$	CH_3OH	basic Al_2O_3	60/20	100	64	470	7.3	99
$RhCl[P(C_6H_5)_3]_3$	CH_3OH	TED	>200/48	100	5	120	24	76
$RuCl_2[P(CH_3)_3]_4$	$scCO_2$	$CH_3OH + N(C_2H_5)_3$	80/125	80	64	3500	55	72
$MnPd(CO_3)(dppm)_2Br$	C_2H_5OH	$N(C_2H_5)_3$	6/6	130	na	na	7	103

Scheme 6. The Outline Mechanism Suggested[88] for the Hydrogenation of CO_2 to CO, CH_3OH, and CH_4



suggesting that methanol hydrogenation was responsible for CH_4 formation (Scheme 6).

A two-step process for methane production from CO_2/H_2 reported by Vaska et al.[90] involved the hydrogenation of CO_2 and ammonia to formamide followed by catalytic and thermal hydrogenation and decomposition to NH_3, CO_2, CO, carbon, water, CH_4, $HCONHCH_3$, and DMF. The route to CH_4 is not clear, but the route to the substituted formamides is discussed in section VI.E.

IV. Producing Alkyl Formates from Alcohols

Methyl formate is primarily used for the industrial synthesis of formic acid and DMF. Other uses include production of foundry molds, solvents, insect control agents,[49] and possibly, in the future, isomerization to acetic acid.[91,92] There are a number of applications of other alkyl formate esters in the fragrance industry and as raw materials for the chemical industry.[16] Methyl formate can be produced by the base-catalyzed carbonylation of methanol with CO, the currently used industrial process, by methanol dehydrogenation,[93] or by the hydrogenation of CO_2 in the presence of methanol (eq 19):

$$CO_2(aq) + H_2(aq) + CH_3OH(l) \rightarrow HCO_2CH_3(l) + H_2O(l) \quad (19)$$

$$\Delta G° = -5.28 \text{ kJ/mol}; \Delta H° = -15.3 \text{ kJ/mol}; \Delta S° = -33.6 \text{ J/(mol K)}$$

Homogeneous catalysis of this reaction was first reported in 1972 by the group of Vol'pin.[94] Catalysts now known to be active (Table 3) include anionic carbonyl complexes and the groups 8–10 metal phosphine complexes which are also catalysts for formic acid production (eq 11). Both types of catalyst have been tested without a basic cocatalyst with resulting complete selectivity for formate ester, but the yields have been quite low.[72,80,95,96] The phosphine complexes with basic cocatalysts give mixtures of formate salts and formate ester. Strictly speaking, the role of the base is catalytic in nature, but the yield of alkyl formate is always less than the amount of base charged. Effective cocatalysts include tertiary amines, among which the best are $N(CH_3)_3$, $N(C_2H_5)_3$, and especially cyclic tertiary amines.[76,97,98] Group 1 and 2 metal hydroxides and alkoxides can be used,[56] but in general particularly strong or weak bases are less effective.[76] Lodge et al.[99] claimed that complete selectivity for formate ester rather than formic acid can be obtained using insoluble metal oxides as bases but did not determine the formic acid content of the solid products. Kolomnikov et al.[94] used a Lewis acid cocatalyst.

All research reports describe reactions with methanol. Ethanol and propanol react more slowly,[76,95,97] possibly because of a lower rate of thermal esterification for higher alcohols.[76] However, Darensbourg et al.[80] discounted this explanation because they found that the product of thermal esterification with 1:1 CH_3OH:C_2H_5OH was a 1:1 mixture of HCO_2CH_3 and $HCO_2C_2H_5$ in a reaction time insufficient for the interesterification equilibrium to be attained. They

Table 4. Homogeneous Hydrogenation of CO_2 and Alkyl Halides to Alkyl Formates

catalyst precursor	solvent	reagents	P_{H_2/CO_2} (atm)	T (°C)	conversion (%)	TON	ref
$RuCl_2[P(C_6H_5)_3]_4$, $IrCl(CO)[P(C_6H_5)_3]_2$, or $OsHCl(CO)[P(C_6H_5)_3]_3$	benzene	CH_3I	30/30	100	1–5	1–5	94
$[Cr_2(\mu\text{-}H)(CO)_{10}]^-$	THF	$n\text{-}C_4H_9Cl + NaHCO_3$	20/20	150	47	~15	100
$WCl(CO)_5^-$	THF	$n\text{-}C_8H_{17}Cl + NaOCH_3$	20/20	150	64	~15	100

suggested that the slower reaction with ethanol was due to the greater metal binding ability of ethanol compared to methanol, which allowed the alcohol to compete effectively with H_2 for a binding site on the metal. The slow reaction of higher alcohols was a motivation for research into the corresponding reactions of alkyl halides with CO_2 and H_2, to produce the higher alkyl formates (section V).[100]

Preliminary results[72] have shown that high yields of methyl formate can be obtained in $scCO_2$ (Table 3) or in methanol under $scCO_2$.

The temperature effect was studied by Phala et al.[76] and discussed in terms of the two-step mechanism via formic acid (section IV.B). For the catalyst $RhCl[P(C_6H_5)_3]_3$, temperatures higher than 125 °C caused catalyst decomposition while at temperatures below 100 °C the esterification of formic acid was too slow.

Decomposition of the ester to alcohol and CO catalyzed by transition metal complexes[101] could be a problem in some systems.

A. Via Carbon Monoxide

In the presence of alkoxide ion or hydrogen gas, the carbonylation of alcohol gives alkyl formate rather than or in addition to carboxylic acids (eq 20).[104] Thus the mechanism for reaction 19 could be

$$ROH + CO \rightarrow RO_2CH \qquad (20)$$

the generation of CO by the reverse WGSR followed by the carbonylation of alcohol. Because some of the anionic carbonyl catalysts noted in Table 3 are also known to be active for the carbonylation of methanol to methyl formate,[96] this mechanism deserves consideration. However, for those catalysts the carbonylation mechanism was ruled out by Darensbourg et al.[80,96,105] for a number of reasons, including the observation that the use of $W(O_2CH)(^{13}CO)_5^-$ as catalyst gave $H^{12}CO_2CH_3$.

B. Via Formic Acid

This mechanism has two steps; the hydrogenation of CO_2 to formic acid (eq 11) and its subsequent thermal esterification (eq 21):

$$HCO_2H + ROH \rightarrow HCO_2R + H_2O \qquad (21)$$

This sequence was proposed by Darensbourg[80] for a system in which the esterification step was much faster than the hydrogenation step, so that formic acid was not observed. Formic acid was observed as an intermediate by Sugita et al. in the reaction catalyzed by $RhCl[P(C_6H_5)_3]_3$ in methanol in the presence of an amine.[76] In this case and in similar systems[72] the ammonium formate salt reaches equilibrium concentration very quickly, while the amount of ester increases more slowly. The transition metal catalyst for formic acid production is not a catalyst for the second step.[72,76] The base is necessary for high conversions to formic acid in the hydrogenation step (see section II), even though it inhibits the esterification step.[72] The low effectiveness of more weakly or strongly basic amines could be due to reduced rates of formic acid production or esterification, respectively.[76]

Note that with any catalyst, the addition of alcohol could significantly alter the mechanism of CO_2 hydrogenation to formic acid. For example, some ruthenium formate complexes are converted to alkyl carbonates by alcohols.[106,107] Thus an alkyl carbonate reduction mechanism could occur (section II.B).

C. Methanolysis

The direct methanolysis of formate complex intermediates (eq 22) is directly comparable to the hydrolysis mechanism for formic acid production (Scheme 3). This mechanism was proposed by Kolomnikov et al.[94] for Ru and Ir phosphine catalysts, while it was ruled out by Darensbourg et al.[80] for Cr and W anionic carbonyl catalysts because the isolated metal formate complex $M(O_2CH)(CO)_5^-$ (M = Cr, W) did not react with methanol to yield methyl formate.

$$MO_2CH + ROH \rightarrow MOH + HCO_2R \qquad (22)$$

Hydroxycarbonyl complex intermediates could undergo a similar reaction, generating an alkoxycarbonyl complex (eq 23).

$$MCO_2H + ROH \rightarrow MCO_2R + H_2O \qquad (23)$$

This is the equivalent of an esterification of the hydroxycarbonyl complex. The liberation of alkyl formate would next require reductive elimination, protonation, or hydrogenolysis. The dialkyloxalates observed by Denise and Sneeden[83] could have arisen by reductive elimination from an $M(CO_2R)_2$ complex, or by reductive elimination of oxalic acid from $M(CO_2H)_2$ followed by esterification. However, such complexes and the resulting oxalate products could also have been produced by methoxide attack on carbonyl ligands.[108] Thus the oxalate products could be consistent with the methanolysis mechanism or the methanol carbonylation mechanism (section IV.A).

V. Producing Alkyl Formates from Alkyl Halides

Formate esters can be made from CO_2, H_2, and alkyl halides (eq 24) in a reaction reminiscent of that with alcohols:

$$H_2 + CO_2 + RX \rightarrow HCO_2R + HX \qquad (24)$$

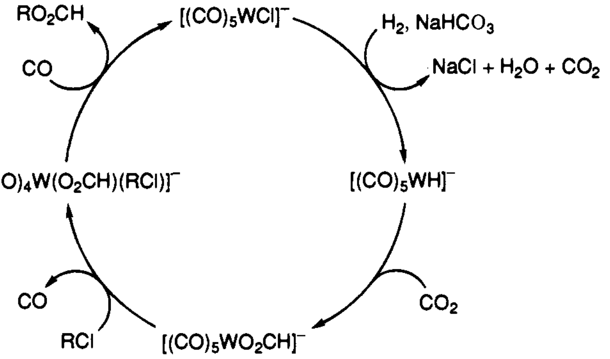
The reaction was first reported by Kolomnikov et al.,[94] who used methyl iodide in benzene with Ru^{II}, Ir^{I}, and Os^{II} phosphine complexes (Table 4). Darens-

Table 5. Production of Formamides from Amines and CO_2

catalyst	R[a]	solvent	P_{H_2/CO_2} (atm)	T (°C)	t (h)	TON	TOF (h^{-1})	yield (%)[b]	ref
$Pd(CO_3)[P(C_6H_5)_3]_2$	CH_3	benzene	28/28	100	17	120	7	60	111
$CdCl_2[P(C_6H_5)_3]_2$	CH_3	benzene	28/28	125	17	10.5	0.6	4	112
$RuCl_3$/dppe/$Al(C_2H_5)_3$	CH_3	hexane	29/29	130	6	3400	570	73	113
$RuCl_2[P(C_6H_5)_3]_4$	CH_3	hexane	29/29	130	6	2650	440	51	113
$PdCl_2/KHCO_3$	CH_3	MC	80/40	170	1.5	34	23	99	54
$RhCl[P(C_6H_5)_3]_3$	CH_3	MC	80/40	150	5	36	7	65	114
$Pt_2(dppm)_3$	CH_3	toluene	67–94/10–12	75	24	1460	61	na	116
$Pt_2(dppm)_3$	CH_3	toluene	114[c]	100	24	1375	57	na	110
$Pt_2(dppm)_3$	CH_3	toluene	1[c]	25	24	8.7	0.4	na	110
$IrCl(CO)[P(C_6H_5)_3]_2$	H	CH_3OH	50–68/13–17	125	240	1145	5	na	90
$RuCl_2[P(CH_3)_3]_4$	CH_3	$scCO_2$	80/130	100	37	370000	10000	76	115

[a] R group in NHR_2. [b] Based on amine. [c] Total pressure.

Scheme 7. The Mechanism Proposed[100] for the Production of Alkyl Formate from Alkyl Halide, CO_2, H_2, and $NaHCO_3$

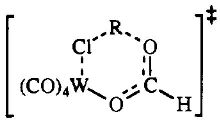


bourg and Ovalles[100] used anionic metal carbonyl catalysts and basic salts to effect the reaction of higher alkyl halides. The most effective salts had high basicity and at least some solubility. In the absence of base, no esters were obtained. Obviously the bases have a thermodynamic role in trapping the evolved hydrohalic acid. Because $NaHCO_3$, which was used as the base, liberates CO_2 upon protonation, there was no net consumption of CO_2. Alkyl chlorides were found to be more reactive than the bromide or iodide analogues, consistent with the greater stability of the tungsten bromide or iodide intermediate, which inhibits formation of the catalytically active metal hydride in the catalytic cycle (Scheme 7). Alcohols and alkanes were obtained as undesired byproducts from the hydrolysis of the product formate esters and from reaction 25, respectively. With $WCl(CO)_5^-$ and

$$MH(CO)_5^- + RX \rightarrow MX(CO)_5^- + RH \quad (25)$$

$NaOCH_3$, hydrogen gas was not needed for the production of alkyl formate; sufficient hydrogen could be obtained by β-hydrogen abstraction reactions of the methoxide ligand after coordination to the W center.

The mechanism for reaction 24 proposed by Darensbourg and Ovalles[100] is shown in Scheme 7. The kinetics were consistent with the rate-determining step being formation of the hydride intermediate.[16,100] In the absence of RX, the tungsten chloride complex is at least partly converted to the formate complex, which itself is catalytically active. The formate complex was shown to react stoichiometrically with alkyl halide, giving the halide complex and the free formate ester, the kinetics of this transformation being consistent with either a concerted process



or the oxidative addition of alkyl halide to a site liberated by CO loss, followed by reductive elimination of alkyl formate.

VI. Producing Formamides or Methylamines from Amines

Formamides, particularly *N*,*N*-dimethylformamide (DMF), are useful polar solvents. DMF is prepared industrially (250000 ton/year) by carbonylation of dimethylamine in the presence of methanol.[109] The synthesis of formamides from dialkylamines, CO_2, and H_2 was first discovered by Farlow and Adkins[50] who used Raney nickel as the catalyst (eq 26, thermodynamic data[110] given for R = CH_3, aqueous reactants and liquid products):

$$CO_2 + NHR_2 + H_2 \rightarrow HCONR_2 + H_2O \quad (26)$$

$$\Delta G° = -0.75\ \text{kJ/mol};\ \Delta H° = -36.3\ \text{kJ/mol};\ \Delta S° = -119\ \text{J/(mol K)}$$

The enthalpy of the reaction is not as favorable as the production of ammonium formate salts (eq 14). The difference is the enthalpy of dehydration (eq 27).

$$[NH_2(CH_3)_2]^+(aq) + [HCO_2]^-(aq) \rightarrow HCON(CH_3)_2(l) + H_2O(l) \quad (27)$$

$$\Delta H° = 21.1\ \text{kJ/mol}$$

The enthalpy of DMF production is more favorable than that for methyl formate (eq 19).

Homogeneous catalysis of this reaction, historically the first homogeneously catalyzed CO_2 hydrogenation, was reported by Haynes et al. in 1970.[111,112] Catalysts for reaction 26 are similar to those for the production of formic acid or alkyl formates: chloro(phosphine) complexes of the metals of groups 8 to 10 (Table 5). Kiso and Saeki[113] found that a chelating diphosphine ligand was more effective than monodentate phosphine ligands. Reusing portions of a product mixture and adding fresh amine can increase the TON.[111] Amines used as substrates include ammonia[72,90] and primary,[72,111] and secondary alkylamines, especially dimethylamine. Particularly bulky dialkylamines such as dicyclohexylamine are not converted.[72] Additional base such as potassium salts or tertiary amines can increase the yield of amide,[54] a fact which circumstantially supports the formate mechanism to be described below. Effective solvents include saturated or aromatic hydrocarbons, neat $NH(CH_3)_2$, $N(C_2H_5)_3$,[113] and a benzene/methyl cellosolve mixture.[54,114] Jessop et al.[115] found very high yields in $scCO_2$, far higher than those so far reported in liquid solvents (see section VIII).

Schreiner et al.[116] found that DMF suffered partial decomposition at 150 °C to CO and $NH(CH_3)_2$, but this was suppressed by 100 atm of H_2.

Overreduction yields methylamines, the thermodynamically favored products (eq 28), which have been observed[116] or suspected[72,90] in some systems.

$$CO_2(aq) + 3H_2(aq) + NH(CH_3)_2(aq) \rightarrow N(CH_3)_3(l) + 2H_2O(l) \quad (28)$$

$$\Delta G^\circ = -110.1 \text{ kJ/mol}; \Delta H^\circ = -147.4 \text{ kJ/mol}; \Delta S^\circ = -125 \text{ J/(mol K)}$$

A. Via Carbon Monoxide

The catalytic carbonylation of dialkylamine by reverse WGSR-generated CO is a possible mechanism. Because homogeneous catalysts for amine carbonylation include late transition metal carbonyl and phosphine complexes,[117] it is important that mechanistic studies of reaction 26 include experiments designed to test for this mechanism. For example, this mechanism was ruled out by Haynes et al.,[111] for $RhCl[P(C_6H_5)_3]_3$ as catalyst, on the grounds that the catalyst would have been converted by CO to a carbonyl complex, which was not detected among the inorganic products.

B. Via Formic Acid

The hydrogenation of CO_2 and amine to ammonium formate, followed by dehydration (eq 29, cf. eq 27), may turn out to be the most common mechanism. The dehydration of ammonium carboxylates is known to proceed thermally or with acid catalysis. The carboxylic acid itself, if present in excess, is sufficient to catalyze the reaction.[118,119] The uncatalyzed thermal condensation of dimethylamine and formic acid is known to proceed at 100 °C.[120] Thermal condensation of an ammonium carbamate with formic acid would also generate the formamide.[121]

$$H_2 + CO_2 + NHR_2 \rightarrow [NH_2R_2][HCO_2] \rightarrow HCONR_2 + H_2O \quad (29)$$

This mechanism was proposed by the group of Sugita[54] for the $PdCl_2/KHCO_3$ system because potassium formate was observed among the products. However, they tentatively rejected the mechanism for the $RhCl[P(C_6H_5)_3]_3$ system for weak reasons.[114] Jessop et al.[115] proposed this mechanism for the $RuCl_2[P(CH_3)_3]_4$ catalyst in $scCO_2$ because formic acid was produced rapidly at the start of the reaction and thereafter was consumed while DMF was generated (Figure 1).

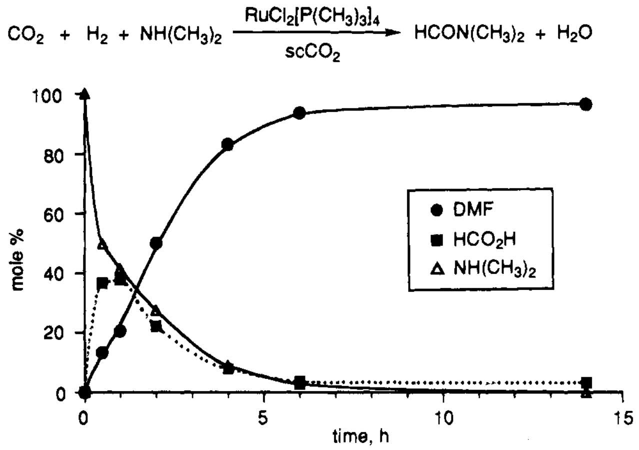


Figure 1. The composition of the product mixture as a function of reaction time for the reaction of $NH(CH_3)_2$ (10 mmol, introduced as the carbamate salt), H_2 (80 atm), and $scCO_2$ (130 atm) at 100 °C catalyzed by $RuCl_2[P(CH_3)_3]_4$ (2.5 μmol). (Reprinted from ref 115. Copyright 1994 American Chemical Society.)

Note that with any catalyst, the addition of a nontertiary amine could significantly alter the mechanism of CO_2 hydrogenation to formic acid. For example, some Ru formate complexes are converted to carbamate complexes by secondary amines,[107] and such conversion could alter the catalytic cycles of related Ru catalysts.

C. Aminolysis

The direct aminolysis of formate complex intermediates (eq 30) is analogous to the hydrolysis mechanism for formic acid production (Scheme 3) and the alcoholysis mechanism for alkyl formate production (eq 22). This mechanism was proposed by Kudo[54] for the $PdCl_2$ catalyst without evidence.

$$MO_2CH + NHR_2 \rightarrow MOH + HCONR_2 \quad (30)$$

Hydroxycarbonyl complex intermediates could undergo a similar reaction, generating carbamoyl complexes (eq 31). The liberation of amide would next require reductive elimination, protonation, or hydrogenolysis.

$$MCO_2H + NHR_2 \rightarrow MCONR_2 + H_2O \quad (31)$$

Note that both mechanisms above require that the proton from the amine ends up in the water product, while the formate proton of the formamide product comes from H_2 gas directly or via metal hydride. Thus use of D_2 gas and $NH(CH_3)_2$ should produce DMF-d_1. However, DMF-d_0 was obtained by Haynes et al.[111] using $IrCl(CO)[P(C_6H_5)_3]_2$, $NH(CH_3)_2$, and D_2. The result has been interpreted as rapid hydrogen exchange between the Ir hydride and dimethylamine followed by the reaction of the hydride and CO_2. Aminolysis of the resulting iridium formate gives DMF and iridium hydroxide (eq 30). With this scrambling, the labeling result becomes consistent with any mechanism.

D. Via Carbamates or Carbonates

Carbon dioxide reacts with ammonia and primary or secondary amines to form carbamic acids and the corresponding ammonium carbamates (eqs 32 and 33, R = H or alkyl):[122,123]

$$NHR_2 + CO_2 \rightleftharpoons HO_2CNR_2 \quad (32)$$

$$HO_2CNR_2 + NHR_2 \rightleftharpoons [NH_2R_2][O_2CNR_2] \quad (33)$$

Metal-catalyzed reduction of a carbamic acid would generate a formamide

$$HO_2CNR_2 + M \rightarrow M(H)(O_2CNR_2) \xrightarrow{H_2} M + HCONR_2 + H_2O \quad (34)$$

but reaction of H_2 with Ru carbamates failed to yield formamides.[107]

Dehydration of ammonium carbamates generates substituted ureas (eq 35):

$$[NH_2R_2][O_2CNR_2] \rightarrow (R_2N)_2CO + H_2O \quad (35)$$

which have been observed during the heterogeneous hydrogenation of CO_2 in the presence of primary amines.[50] Substituted ureas are not likely to be intermediates for the synthesis of formamides; Haynes et al.[111] noted that tetramethylurea could not be converted to DMF under the conditions used for the production of DMF from CO_2, H_2, and $NH(CH_3)_2$. There is thus no evidence that reduction via carbamates can lead to formamides.

Reactions of $NH(CH_3)_2$ and H_2 with CO_2, COS, and CS_2 in the presence of $CuCl[P(C_6H_5)_3]_3$ have been reported.[111] From COS, tetramethylurea is obtained, while in the case of CS_2 the reaction stops at the dimethylammonium dimethylthiocarbamate stage. The mechanism of the synthesis of DMF from CO_2 with this catalyst is unknown.

Carbonates are the hydrates of carbamates. Thus, reaction pathways via carbonates are simple variations of those via carbamates or those described in section II.B.

E. Methylamine Formation

Trimethylamine has been detected or suspected as a minor product of the reduction of CO_2 and dimethylamine to DMF.[115,116] The most obvious mechanism is the catalytic hydrogenation of DMF:

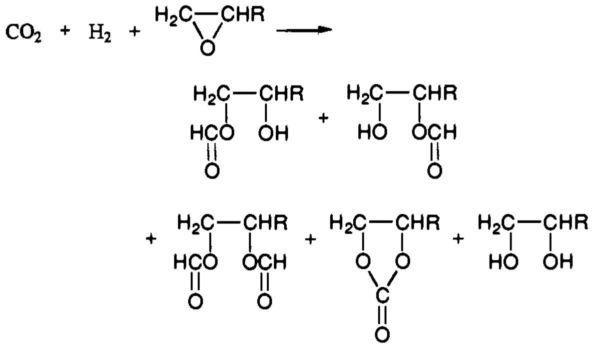
$$HCONR_2 + 2H_2 \rightarrow N(CH_3)R_2 + H_2O \quad (36)$$

Heterogeneously[124] and homogeneously[90,116] catalyzed hydrogenations of amides to alkylamines are known. Schreiner et al.[116] found that phosphine complexes of Ru^{II}, Pt^0, and Pt^{II} are particularly active. Other possible mechanisms for $N(CH_3)R_2$ formation include alkyl group scrambling between two amines or between an amine and an amide. However, Schreiner et al.[116] rejected these mechanisms because NH_2CH_3 was not detected in their system.

Hydrogenation of $HCONH_2$ catalyzed by $IrCl(CO)[P(C_6H_5)_3]_2$ produces *N*-methylformamide, DMF, and other products. Initial hydrogenation of formamide to methylamine followed by alkyl group exchange is suspected as the route for the production of the substituted formamides.[90]

VII. Producing Diols and Diol Formates from Oxiranes

In the absence of H_2, CO_2 reacts with oxiranes and oxetanes to give copolymers[125] and cyclic carbonates.[126–128] Koinuma et al.[129] reported that the reaction of CO_2 with methyloxirane in the presence of H_2 produces 1,2-diols and their formates in addition to the cyclic carbonate (eq 37). The catalysts



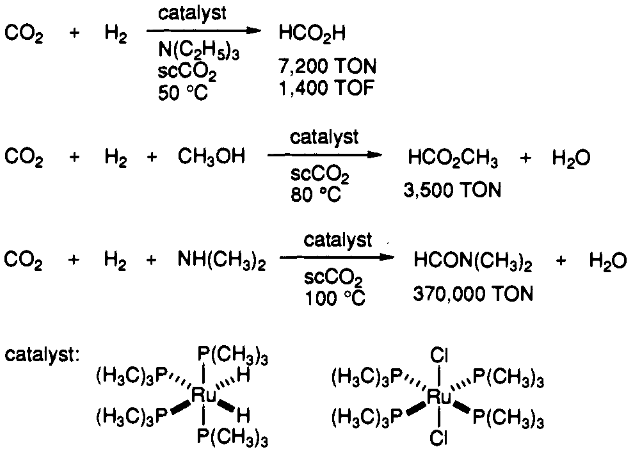
(37)

were chloro(triphenylphosphine) complexes of Ru, Rh, and Co; reactions were at 100 °C for 40 h, with the highest yield of carbonate, 1300 TON, being obtained with $RuCl_2[P(C_6H_5)_3]_3$, and the greatest selectivity (50%) for 1,2-diol formates being obtained at longer reaction times. There was evidence of a significant induction period; increasing the reaction time by 4-fold increased the overall conversion by 26-fold. The cyclic carbonate is the product of insertion of CO_2 into the oxirane, and thus does not require H_2.[126–129] The formate products could result from hydrogenation of the cyclic carbonate,[11] oxirane insertion into a metal–formate bond, or reaction of the oxirane with formic acid. There is insufficient data to determine the correct mechanism. Koinuma et al. favored the oxirane insertion mechanism and discounted the formic acid mechanism because the yields of monoformate esters varied depending on the size of the R group of the oxirane, a trend not expected for the formic acid mechanism.

VIII. Homogeneous Hydrogenation of Supercritical CO_2

As briefly mentioned in preceding sections, recent tests have shown that high yields and rates of reaction can be obtained by using supercritical CO_2 ($scCO_2$) as the reaction medium for its own hydrogenation (Tables 1, 3, and 5). When heated beyond its critical temperature (31 °C),[130] CO_2 becomes supercritical and has densities intermediate between those of liquid and gaseous CO_2. In this supercritical state and preferably at pressures above the critical pressure (73 atm),[130] $scCO_2$ can dissolve a wide range of compounds.[131] Depending on the total pressure, hydrogen can be dissolved in particularly large amounts,[132] making supercritical CO_2 a good medium for its own hydrogenation. For example, hydrogenation to formic acid with the $scCO_2$-soluble catalyst precursor $RuH_2[P(CH_3)_3]_4$ is faster in $scCO_2$ than in

Scheme 8. The Homogeneous Hydrogenation of Supercritical CO_2



liquid solvents such as THF,[60] $N(C_2H_5)_3$, CH_3OH, CH_3CN, or water under otherwise identical conditions (Scheme 8).[72] Preliminary studies of the synthesis of methyl formate in $scCO_2$ or in methanol under $scCO_2$ have shown very high yields (Table 3).[72] Also, with the catalyst precursor $RuCl_2[P(CH_3)_3]_4$ dissolved in $scCO_2$, the syntheses of formic acid (eq 11)[60] or DMF (eq 26)[115] have higher yields than any previously reported for subcritical systems. There are several possible reasons for this, including (a) the high diffusion rates in $scCO_2$ compared to the slow rates of diffusion of H_2 and CO_2 into liquid solvents, (b) the lack of a strong solvation sphere around the metal center in $scCO_2$, or (c) the high concentration of H_2[132] and CO_2 possible in $scCO_2$. The yield of DMF, 370000 TON (Table 5), is the greatest efficiency for any of the reactions described in this review, possibly because of the above favorable factors plus the irreversibility of the reaction under the conditions used.

IX. Concluding Remarks

Most of the products generated by these hydrogenations of CO_2, including formic acid, methyl formate, DMF, and methanol, are made industrially from CO rather than CO_2. We have now seen that high catalytic efficiency can be obtained for many of these reactions of CO_2. In particular, systems with water or $scCO_2$ as reaction media show the most promise, with the highest catalytic efficiency being 370000 TON.[115] The adoption of such processes by industry hinges on market forces, primarily the price of hydrogen. It is possible that future legislative controls on CO_2 emissions will add incentive to the use of CO_2 as a feedstock. At the present stage, homogeneous catalysis is merely a research tool for these reactions; the CO_2 hydrogenation processes in industrial use or future plans involve heterogeneous catalysis. However, the rapidly improving yields described in this review suggest that homogeneously catalyzed CO_2 hydrogenation reactions may emerge as economically viable technologies.

Further basic research emphasizing mechanistic aspects of this chemistry are sorely needed. For most of the systems summarized herein insufficient kinetic data are available to discern the operating mechanisms. The search for new catalysts and processes must rely on a better understanding of the mechanisms of those already discovered.

X. Abbreviations

cod	1,5-cyclooctadiene
dippe	$[(CH_3)_2CH]_2PCH_2CH_2P[CH(CH_3)_2]_2$
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
dppb	$(C_6H_5)_2PCH_2CH_2CH_2CH_2P(C_6H_5)_2$
dppe	$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$
dppm	$(C_6H_5)_2PCH_2P(C_6H_5)_2$
dppp	$(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$
EDTA·H	protonated ethylenediaminetetraacetic acid
L	neutral or anionic ligand
M	metal complex fragment, including transition metal and possibly neutral and anionic ligands
MC	methyl cellosolve
na	not available
nbd	2,5-norbornadiene
NMP	*N*-methyl-2-pyrrolidone
P	pressure
PPN	bis(triphenylphosphine)imminium cation
R	alkyl or aryl group
rt	room temperature
sc	supercritical
t	time
T	temperature
TED	$N(CH_2CH_2)_3N$
THF	tetrahydrofuran
TOF	turnover frequency, TON per hour
TON	turnover number, moles product per mole of catalyst
WGSR	water gas shift reaction (eq 1)

XI. References

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