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Hydrogenation of Carbon Dioxide Catalyzed by Ruthenium Trimethylphosphine Complexes: The Accelerating Effect of Certain Alcohols and Amines

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Abstract: A trace amount of alcohol cocatalyst and a stoichiometric amount of base are required during the hydrogenation of CO_2 to formic acid catalyzed by ruthenium trimethylphosphine complexes. Variation of the choice of alcohol and base causes wide variation in the rate of reaction. Acidic, nonbulky alcohols and triflic acid increase the rate of hydrogenation an order of magnitude above that which can be obtained with traditionally used methanol or water. Similarly, use of DBU rather than NEt_3 increases the rate of reaction by an order of magnitude. Turnover frequencies up to 95 000 h^{-1} have now been obtained, and even higher rates should be possible using the cocatalyst and amine combinations identified herein. Preliminary in situ NMR spectroscopic observations are described, and the possible roles of the alcohol and base are discussed.

Introduction

Carbon dioxide will become increasingly available as a cheap and abundant carbon feedstock as requirements for its trapping from power plants come into play. CO_2 is already used as a reagent for the synthesis of aspirin and carbonates.[1] However, development of highly efficient methods for CO_2 reduction would greatly increase the range of possible products derivable from CO_2. Earlier reports by one of us[2,3] described a very rapid method for the hydrogenation of CO_2 to formic acid, using homogeneous catalysts dissolved in supercritical carbon dioxide. We now report new discoveries which greatly increase the rate of CO_2 hydrogenation.

Ever since the first reports of the homogeneous hydrogenation of CO_2 to formic acid (Table 1, eq 1), the importance of the addition of a base and a protic cocatalyst (usually either water or an alcohol) has been recognized.[2,4−7] At the very least, the base acts to thermodynamically stabilize the formic acid product. In triethylamine, the most commonly used base, the product is a nearly 2:1 mixture.[8−11] The base or its conjugate acid may also play a role in the mechanism.[3,12,13] The water or alcohol, which is needed in catalytic rather than stoichiometric quantities,[5,6,14,15] must play a mechanistic role. However, an extensive screening of the effectiveness of various amines and alcohols has not been previously reported.

The most active catalyst precursors reported for this reaction so far have been Ru(II) trimethylphosphine complexes of the formula $RuX(Y)(PMe_3)_4$ (X, Y = H, Cl, O_2CMe).[2,3,16] We have therefore used the easily prepared, fairly stable, and highly active complex $RuCl(O_2CMe)(PMe_3)_4$ as the catalyst precursor for this study.

$$CO_2 + H_2 \xrightarrow{Ru^{II}\ catalyst} HCO_2H \qquad (1)$$

Herein we report a detailed study of the effect of bases and alcohols which lead to greatly increased rates of hydrogenation

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Table 1. Reports of Homogeneous Hydrogenation of CO_2 to Formic Acid, Presented in Order of Increasing TOF[a]

catalyst precursor	solvent	reagent	$P_{H2}/_{CO2}$, bar	T, °C	TOF, h^{-1}	ref
$[(C_5H_4(CH_2)_2NMe_2)Ru(dppm)]BF_4$	THF		40, 40	80	0.4	12
$[Rh(nbd)(PMe_2Ph)_3]BF_4$	THF	H_2O	48, 48	40	3	6
$RuH_2(PPh_3)_4$	C_6H_6	NEt_3, H_2O	25, 25	rt	4	5
$[Rh(cod)Cl]_2$, dippe	DMSO	NEt_3	40 total	24	11	19
$RuCl_2(PTA)_4$	H_2O	HCO_3^-	60, 60	25	25	20
$RuH_2(PPh_3)_4$	C_6H_6	Na_2CO_3	25, 25	100	42	21
$[Rh(cod)Cl]_2$, dppb	DMSO	NEt_3	20, 20	rt	52	22
$RhCl(PPh_3)_3$	C_6H_6	Na_2CO_3	60, 55	100	58	23
$TpRuH(MeCN)(PPh_3)$	THF	H_2O, NEt_3	25, 25	100	63	15
$[RhCl(cod)]_2$, dppm	DMSO	NEt_3	20, 20	25	79	24
$[Rh(Cy_2PC_2H_4OMe)_2]BPh_4$	MeOH	H_2O, NEt_3	25, 25	55	100	25
$Ru_2(CO)_5(dppm)_2$	Me_2CO	NEt_3	35, 35	rt	207	26
K[Ru(EDTA-H)Cl]	H_2O		3, 17	40	250	27
$RhCl\{P(C_6H_4m\text{-}SO_3Na)_3\}_3$	H_2O	$HNMe_2$	20, 20	rt	287	28
$[RhH(cod)]_4$, dppb	DMSO	NEt_3	40 total	rt	390	29
$PdCl_2$	H_2O	KOH	110, na	160	530	30
$[Ru(Cl_2bpy)_2(H_2O)_2](CF_3SO_3)_2$	EtOH	NEt_3	30, 30	150	625	31
$[Ru(CO)_2Cl_2]_n$	H_2O, ^{i}PrOH	NEt_3	81, 27	80	1,300	32
Rh(dcpb)(hfacac)	DMSO	NEt_3	20, 20	25	1,335	33,34
$RuH_2(PMe_3)_4$	$scCO_2$	NEt_3, MeOH	85, 125	50	1,400	2
$RuCl(OAc)(PMe_3)_4$	$scCO_2$	NEt_3, C_6F_5OH	70, 120	50	95,000	this work

[a] Abbreviations: Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine, cod = 1,5-cyclooctadiene, Cy = cyclohexyl, dcpb = $Cy_2P(CH_2)_4PCy_2$, DMSO = dimethyl sulfoxide, dppm = $Ph_2PCH_2PPh_2$, dppb = $Ph_2PCH_2CH_2CH_2CH_2PPh_2$, dippe = $^iPr_2PCH_2CH_2P^iPr_2$, EDTA-H = monodeprotonated ethylenediaminetetraacetic acid, hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate, nbd = norbornadiene, PTA = 1,3,5-triaza-7-phosphaadamantane, rt = room temperature, TOF = turnover frequency = mol HCO_2H per mol transition metal per h, Tp = hydrotris(pyrazolyl)borate. The TOF values are either initial TOF values or average TOF values, depending on the data available in the source article.

plus interesting clues concerning the role that these reagents play in the hydrogenation mechanism.

Experimental Section

Reagents. Amines, alcohols, solvents, and other liquid reagents were degassed by repeated freeze/pump/thaw cycles and then stored and handled under nitrogen. Toluene was distilled from sodium/benzophenone ketyl under nitrogen.

The $RuCl(OAc)(PMe_3)_4$ catalyst precursor[17] and the salt of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and methylcarbonic acid[18] were prepared by the literature procedures. All the catalytic runs were performed with equipment described in a previous paper.[14] Pressure vessels were loaded under dry nitrogen atmosphere.

Typical Procedure for Liquid-Phase Reactions. Reactions were performed inside glass vials inside a 160-mL high-pressure reaction vessel, which was oven-dried before use. Each glass vial contained a small magnetic stir bar, 5 mmol of amine, 3 μmol of catalyst precursor [$RuCl(OAc)(PMe_3)_4$] and 0.1 mmol of an alcohol. Reactions involving volatile amines were performed in a 31-mL vessel. In either case, the vessel was loaded and closed under a dry N_2 atmosphere in a glovebox. After being removed from the glovebox, the vessel was flushed with H_2 three times and placed in a 50 °C water bath for 30 min to allow for equilibration of the temperature inside the vessel. H_2 gas was then introduced to a pressure of 20 bar at 50 °C. The vessel contents were stirred under these conditions for 1 h. The subsequent introduction of CO_2 (up to a total pressure of 40 bar) was considered the start of the reaction. After the desired reaction time, the vessel was cooled in ice water and then dry ice/acetone until the pressure reached a constant and low value. The vessel was then vented slowly and allowed to thaw to room temperature. The vessel was opened up and $CHCl_3$ (100 μL, 1.25 mmol) was added to the vial contents, to serve as an internal standard. CD_3OD was also added, as needed, to ensure a homogeneous solution. A sample of the solution was dissolved in CD_3OD in an NMR tube and analyzed immediately by ^1H NMR spectroscopy. The yield is expressed in the tables as the ratio of moles of formic acid product per mole of amine used.

Supercritical Phase Hydrogenation of CO_2. A small magnetic stir bar, 15 mmol (2.1 mL) of NEt_3, 0.6 μmol of catalyst precursor [$RuCl(OAc)(PMe_3)_4$], and 0.1 mmol of C_6F_5OH were placed in an oven-dried 31-mL high-pressure vessel and closed under nitrogen. The vessel was then flushed three times with hydrogen and temperature equilibrated in a 50 °C water bath for 1 h at 70 bar H_2. After that, CO_2 was added to a total pressure of 190 bar at 50 °C and reaction was stopped 20 min later and analyzed by the method described above.

Hydrogenation of Carbonate. (a) Without CO_2. The catalyst precursor $RuCl(O_2CMe)(PMe_3)_4$ (3 μmol), DBU-carbonate salt (5 mmol), methanol (0.1 or 10 mmol), and a stir bar were placed in a 31-mL high-pressure vessel under nitrogen. The vessel was then sealed, flushed three times with hydrogen, and kept at 50 °C for 15 min to equilibrate the temperature. The H_2 pressure was then raised to 20 bar and the vessel contents were stirred for 10 h. The reaction was stopped and the contents analyzed as described above for CO_2 hydrogenation.

(b) With CO_2. In otherwise identical experiments, CO_2 (20 bar) was introduced after 1 h of reaction time, and the reaction continued for a further 9 h.

NMR. Multinuclear NMR studies on the ruthenium-containing compounds were performed using a standard broadband 5-mm NMR probe in the appropriate solvents on a 7.01 T Varian VXR NMR spectrometer externally referenced to TMS (^1H) and 85% H_3PO_4 (^{31}P). High-pressure $^{31}P\{^1H\}$ and ^1H NMR spectroscopy were conducted using a 10-mm o.d. 3.5-mm i.d. PEEK NMR cell run unlocked.[35,36] The NMR

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cell was loaded with *cis*-RuCl(OAc)(PMe_3)$_4$ and a 3:1 molar ratio of MeOH:NEt_3 (0.20 mL total) in an inert atmosphere box. The cell was sealed and pressurized with H_2 and in some experiments with H_2 followed by CO_2.

The chemical shifts of the reaction solutions were compared with authentic compounds synthesized from literature methods when possible.

Safety Warning. Operators of high-pressure equipment such as that required for these experiments should take proper precautions, including but not limited to the use of blast shields and pressure-relief mechanisms, to minimize the risk of personal injury.

Results

Effect of Bases. A range of organic and inorganic Brønsted and Lewis bases have been tested for their ability to promote the production of formic acid (Table 2) in the presence of RuCl(O_2CMe)(PMe_3)$_4$ and methanol at 50 °C. Subcritical pressures of CO_2 were used. For the liquid bases, the base itself was the solvent (in addition to 0.1 mmol MeOH). For the solid bases, the reaction was performed twice, once with essentially no solvent (0.1 mmol MeOH) and once with excess MeOH as the solvent. The effectiveness of each base was measured by the yield of formic acid obtained after 1 or 10 h; the yields are reported as moles of formic acid per mol of base. Because the theoretical maximum yield is 1 or more moles of formic acid per mol of base,[3,8] and the majority of the yields obtained in this study were below 0.5, the yield after 1 h should be considered an indication of the ability of the base to promote rapid hydrogenation and not an indication of the eventual yield.

Among the organic bases, those with intermediate basicity (pK_a of conjugate acid between 8 and 12, Table 3) give the greatest yields of formic acid after 1 h. These are triethylamine, tripropylamine, TED (triethylenediamine or 1,4-diazabicyclo-[2.2.2]octane), TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), 2-(diethylamino)ethanol, and especially DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene). Of these, DBU gave by far the greatest rate of reaction, 8 times better than the second best base (TMEDA) and 10 times better than NEt_3, the base used in the previous studies.

None of the other bases resulted in much more than a trace yield of formic acid in the first hour (i.e., ≤0.04 mol acid per mol base). These ineffective bases included all of the inorganic bases regardless of their base strength. In addition, the ineffective bases included a range of organic bases of strengths outside the optimum range identified above (pK_a of conjugate acid 8−12). For example, 1,8-bis(dimethylamino)naphthalene (DMAN), which is a slightly stronger base, and pyridine, diethylaniline, triphenylamine, and $N(CF_2CF_3)_3$, which are weaker bases, were ineffective. The very weak bases (NPh_3 and $N(CF_2CF_3)_3$) are thermodynamically incapable of deprotonating and stabilizing formic acid. The moderately weak bases (e.g., diethylaniline) are only ineffective with alkanol promoters; with more acidic promoters, such amines become effective (vide infra).

Table 2. The Yield of Formic Acid after 1 or 10 h in the Presence of Methanol and Various Bases[a]

base	MeOH, mmol	yield after 1 h	yield after 10 h
triethylamine	0		0.03
	0.1	0.09	0.54
tripropylamine	0.1	0.10	0.70
trioctylamine	0.1	0.04	0.07
N,*N*-diethylaniline	0.1	0.002	0.03
triphenylamine	0.1	0.01	0.009
	10	0.01	0.02
$N(CF_2CF_3)_3$	0.1	0	0
TMEDA	0.1	0.12	0.63
DMAN	0.1	0.02	0.03
	10	0.02	0.03
TED	0.1	0.10	0.10
	10	0.08	0.09
quinuclidine	0.1	0.01	0.007
	10	0.01	0.007
DBU	0.1	0.92	1.42
pyridine	0.1	0	0
2,2′-bipyridyl	0.1	0.03	0.04
	10	0.03	0.04
4-methyl morpholine *N*-oxide	0.1	0.02	0.009
	10	0.02	0.01
4-(dimethylamino)pyridine	0.1	0.01	0.009
	10	0.01	0.09
tetrabutylammonium bromide	0.1	0.01	0.02
	10	0.01	0.02
cinchonine	0.1	0.01	0.01
	10	0.01	0.009
DMF	0.1	0.02	0.02
N,*N*-diethylethanolamine	0.1	0.10	0.27
NaOAc	0.1	0.006	0.009
	10	0.01	0.008
NaOH	0.1	0.008	0.008
KOH	0.1	0.01	0.007
	10	0.001	0.001
Na_2CO_3	0.1	0.02	0.01
	10	0.01	0.01
K_2CO_3	0.1	0.02	0.02
	10	0.009	0.008
$(NH_4)_2CO_3$	0.1	0.01	0.01
	10	0.002	0.002
$NaHCO_3$	0.1	0.02	0.01
	10	0.001	0.001

[a] Conditions: 20 bar CO_2, 20 bar H_2, 5 mmol base, 3 μmol RuCl(O_2CMe)(PMe_3)$_4$, 50 °C. Abbreviations: DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene), DMAN = 1,8-bis(dimethylamino)naphthalene, DMF = *N*,*N*-dimethylformamide, TED = triethylenediamine or 1,4-diazabicyclo[2.2.2]octane, TMEDA = N,N,N′,N′-tetramethylethylenediamine.

Solubility limitations are blamed for the poor performance of the stronger bases (pK_a ≥ 12). DMAN and many of the inorganic bases (all of which were ineffective) are thermodynamically competent to deprotonate and stabilize formic acid. However, they all have very limited solubility in methanol. Similar problems exist with the three organic bases of intermediate basicity (pK_a 8−12), quinuclidine, cinchonine, and trioctylamine, which did not effectively promote the production of formic acid. Trioctylamine was immiscible with methanol, which may have adversely affected its performance, and cinchonine and quinuclidine are solids. Solid bases were generally ineffective, even if the amount of methanol was increased from 0.1 mmol to 10 mmol. With the solid inorganic bases in particular, the yield decreased considerably when the methanol volume was increased. Only one base (4-(dimethylamino)pyridine) performed significantly better in a larger amount of methanol, but even then the yield was not very high.

Although quinuclidine was ineffective for this Ru-catalyzed hydrogenation in MeOH, Hutschka et al.[37] found that qui-

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Table 3. Dissociation Constants for the Conjugate Acids of the Bases Mentioned in This Study[a]

base	pK_a (aqueous scale)	pK_a (DMSO scale)	pK_a (THF scale)
hydroxide	15.7[b]	31.2[c]	44.5
DMAN	12.3[d]	7.5	11.1
DBU	12[e]		
quinuclidine	11.1[f]	9.8	13.5
TMEDA	10.8		
triethylamine	10.7	9.0	12.5[g]
tripropylamine	10.7		12.7[h]
trioctylamine	10.5[i]		
carbonate	10.3		
$Et_2NCH_2CH_2OH$	10.1[j]		
cinchonine	9.9		
TED	8.6	8.9	12.5
N,*N*-diethylaniline	6.6	∼2.5[k]	∼5.8
bicarbonate	6.4		
4-(dimethylamino)pyridine	6.1		
pyridine	5.2	3.5	6.8
acetate	4.8	12.6	26.1
2,2′-bipyridyl	4.4		
triphenylamine	∼2.2[l]		
DMF	−1.2[m]		2.1[h]
$N(CF_2CF_3)_3$	∼−15.7[l]		

[a] All data at 20−25 °C. Aqueous and DMSO scale data from refs 38 and 39, respectively, except as noted. THF scale data calculated by the equations of Morris in ref 40 from the DMSO data except as noted. [b] Reference 41. [c] Reference 42. [d] Reference 43. [e] Reference 44. [f] Reference 45. [g] Reference 40. [h] Calculated from MeCN scale data of ref 39 using the equations of Morris in ref 40. [i] Reference 46. [j] Reference 47. [k] This is the pK_a for *N*,*N*-di*methyl*aniline from ref 42. [l] Predicted using the tables in ref 48. [m] Reference 49.

nuclidine was more effective than NEt_3 in promoting the [Rh(hfacac)(dppe)]-catalyzed CO_2 hydrogenation in DMSO. They proposed that the lack of steric hindrance around the basic site of quinuclidine rendered it more capable of assisting in the rate-limiting elimination of formic acid from a Rh formate or formic acid complex intermediate.

Essentially no formic acid was obtained if Lewis bases and other compounds which have essentially no basic character were used in place of triethylamine. Such compounds include 4-methyl morpholine *N*-oxide, tetrabutylammonium bromide, and *N*,*N*-dimethylformamide (DMF).

Effect of Alcohols. A range of alcohols and other cocatalysts have been tested for their ability to promote the production of formic acid (Table 4) in the presence of $RuCl(O_2CMe)(PMe_3)_4$ and triethylamine at 50 °C. The yield of formic acid was determined after 1 and 10 h in each case. The amine itself was the solvent.

An alcohol or other proton source is required for this reaction. Essentially no formic acid is obtained in NEt_3 in the absence of an alcohol (Table 2). We[14] and others[5] have shown that only substoichiometric amounts of alcohol are required.

Although water and methanol have traditionally been used in the role of cocatalyst for CO_2 hydrogenation, we have found that more acidic alcohols are far more effective (Table 4 and Figure 1). In fact, *the alcohols which are highly effective are those which have aqueous scale pK_a's below that of the protonated amine* (Figure 1, Tables 3−5). If NEt_3 is the amine, then the effective alcohols are phenol, hexafluoro-2-propanol, pentafluorophenol, and especially triflic acid. The yield of formic acid after 1 h with C_6F_5OH/NEt_3 was 8-fold greater than that obtained with $MeOH/NEt_3$. It is not sufficient to use any relatively strong Brønsted acid: HBF_4 is not nearly as effective

Table 4. The Yield of Formic Acid after 1 or 10 h in the Presence of Various Additives or Cocatalysts[a]

base	additive	yield after 1 h	yield after 10 h
triethylamine	THF	0.03	0.04
	C_6H_6	0.02	0.02
	DMSO	0.11	0.26
	MeCN	0.09	0.13
	H_2O	0.06	0.28
	MeOH	0.09	0.54
	EtOH	0.05	0.76
	$HOCH_2CH_2OH$	0.10	0.48
	t-BuOH	0.06	0.16
	i-PrOH	0.11	0.22
	PhOH	0.21	0.97
	2,6-^{t}Bu$_2$C$_6$H$_3$OH	0.001	0.001
	$(CF_3)_2CHOH$	0.47	1.32
	3,5-$(F_3C)_2C_6H_3OH$	0.73	
	2,4-$(O_2N)_2C_6H_3OH$	0.72	
	C_6Cl_5OH	0.32	
	C_6F_5OH	0.66	1.54
	HBF_4	0.19	
	CF_3SO_3H	1.09	
tripropylamine	MeOH	0.10	0.70
	C_6F_5OH	1.00	1.68
trioctylamine	MeOH	0.04	0.07
	C_6F_5OH	0.07	0.13
N,*N*-diethylaniline	MeOH	0.002	0.03
	PhOH	0.001	0.002
	2,6-^{t}Bu$_2$C$_6$H$_3$OH	0	0
	2,4,6-^{t}Bu$_2$C$_6$H$_3$OH	0	0
	3,5-$(F_3C)_2C_6H_3OH$	0.46	
	2,4-$(O_2N)_2C_6H_3OH$	0.23	
	$(CF_3)_2CHOH$	0.02	0.05
	C_6Cl_5OH	0.33	
	C_6F_5OH	0.10	0.44
	CF_3SO_3H	0.50	
triphenylamine	MeOH	0.01	0.009
	C_6F_5OH	0.004	0.03
$N(CF_2CF_3)_3$	MeOH	0	0
TMEDA	MeOH	0.12	0.63
	C_6F_5OH	0.10	1.47
DMAN	MeOH	0.02	0.03
	C_6F_5OH	0.04	0.09
TED	MeOH	0.10	0.10
	C_6F_5OH	0.07	0.19
quinuclidine	MeOH	0.01	0.007
	C_6F_5OH	0.04	0.14
DBU	MeOH	0.92	1.42
	C_6F_5OH	1.36	1.60
pyridine	MeOH	0	0
	3,5-$(F_3C)_2C_6H_3OH$	0.13	
	2,4-$(O_2N)_2C_6H_3OH$	0.08	
	C_6Cl_5OH	0.14	
	C_6F_5OH	0.02	0.09
	CF_3SO_3H	0.09	
2,2′-bipyridyl	MeOH	0.03	0.04
	C_6F_5OH	0.06	0.09
4-methylmorpholine-*N*-oxide	MeOH	0.02	0.009
	C_6F_5OH	0.05	0.09
4-(dimethylamino)pyridine	MeOH	0.01	0.009
	C_6F_5OH	0.003	0.02
$[NBu_4]Br$	MeOH	0.01	0.02
	C_6F_5OH	0.07	0.16
cinchonine	MeOH	0.01	0.01
	C_6F_5OH	0.008	0.01
DMF	MeOH	0.02	0.02
	C_6F_5OH	0.009	0.02
N,*N*-diethylethanolamine	MeOH	0.10	0.27
	C_6F_5OH	0.12	0.88

[a] Conditions: 20 bar CO_2, 20 bar H_2, 0.1 mmol additive, 5 mmol base, 3 μmol $RuCl(O_2CMe)(PMe_3)_4$, 50 °C.

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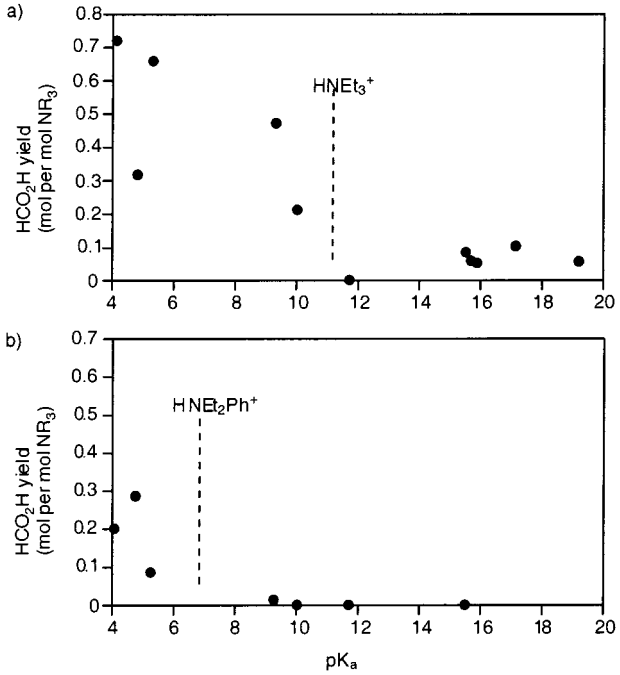

Figure 1. The dependence of the yield of formic acid per mol of amine on the pK_a (aqueous scale) of the alcohol, (a) using NEt_3, (b) using NEt_2Ph. The pK_a's of the protonated amines are shown as dashed lines. Conditions: 1 h reaction time, 3 μmol Ru, 0.1 mmol ROH, 5 mmol amine, 20 bar H_2, total pressure 40 bar (balance CO_2).

Table 5. Dissociation Constants for Cocatalysts (Alcohols and Related Acids) Mentioned in This Study[a]

acid	pK_a (aqueous scale)	pK_a (DMSO scale)	pK_a (THF scale)
t-BuOH	19.2[b]	32.2	49.2
i-PrOH	17.1[b]	30.3	46.9
EtOH	15.9[b]	29.8[c]	46.4
H_2O	15.7[d]	31.2	48.0
MeOH	15.5[b]	29.0	45.4
$HOCH_2CH_2OH$	14.2		
2,4,6-^{t}Bu$_2$C$_6$H$_3$OH	~12.2[e]		
2,6-^{t}Bu$_2$C$_6$H$_3$OH	~11.7[e]	16.9	31.2
PhOH	10.0	18.0	32.5
$(CF_3)_2CHOH$	9.4		
C_6F_5OH	5.5[b]		
C_6Cl_5OH	4.8[f]	7.0[g]	19.5
2,4-$(O_2N)_2C_6H_3OH$	4.1	5.2[g]	17.4
HCO_2H	3.8	10.3[g]	23.4
HBF_4	0.5[h]		0[j]
CF_3SO_3H	−11[k]	diss[g,m]	

[a] All data at 20−25 °C. Aqueous and DMSO scale data from refs 38 and 42 except as noted. THF scale data calculated using the equations of Morris in ref 40 from the DMSO data except as noted. [b] Reference 51. [c] Reference 52. [d] Reference 41. [e] Estimated in ref 53. [f] Reference 54. [g] Reference 39. [h] Reference 55. [j] Reference 56. [k] Reference 57. [m] Completely dissociated.

as the acidic alcohols. Also, a sterically encumbered alcohol, 2,6-di-*tert*-butylphenol, was less effective than either phenol or methanol even though its pK_a lies between those of methanol and phenol.

The general rule stated above is evident in the results with other amines as well. For example, the conjugate acid of *N*,*N*-diethylaniline has a pK_a (aqueous scale) of 6.6. The alcohols with pK_a's lower than that were effective in promoting formic acid synthesis in the presence of *N*,*N*-diethylaniline (Figure 1). Triflic acid was again the most effective additive. The yields of formic acid obtained with triflic acid or phenols with electron withdrawing groups were over 2 orders of magnitude higher than those obtained with the less acidic PhOH or MeOH. With pyridine as the base, another difficulty was encountered. None of the alcohols used in this study have a pK_a below that of protonated pyridine (5.3). Even dinitrophenol, the most acidic alcohol used, gave only a small yield of formic acid when used in conjunction with pyridine.

The discovery of the strong promoting effect of small amounts of pentafluorophenol has now been applied to the hydrogenation of supercritical CO_2 (actually a supercritical mixture of CO_2 and H_2).[50] The reaction was performed for 20 min at 50 °C with 0.6 μmol catalyst precursor, giving a yield of 19 mmol formic acid, which represents a TOF of 95 000 h^{-1}. This rate of reaction is higher than any reported in the literature for CO_2 hydrogenation (Table 1).

Effect of "Nonprotic" Additives. Additives which are incapable of serving as a hydrogen bond donor or as a strong ligand, such as THF and benzene, had no favorable effect on the rate of the hydrogenation (Table 4). However, DMSO and MeCN, which are nonprotic but are known to be relatively strong ligands for Ru(II) complexes,[58] enhanced the rate of the hydrogenation. The enhancement with MeCN was quite modest, but as we have noticed previously with these catalysts,[3,14] DMSO had a very strong effect. The rate enhancement over that in the presence of no additive was 9-fold for DMSO, compared to 18-fold for MeOH and 51-fold for C_6F_5OH. DMSO has also been used with Rh catalysts.[19,22,29,34]

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Table 6. Effect of Combinations of Additives on the Yield of Formic Acid after 1 or 10 h in the Presence of Triethylamine[a]

polar aprotic additive (mmol)	other additive (mmol)	yield after 1 h	yield after 10 h
none	none		0.03
	THF (0.1)	0.03	0.04
	benzene (0.1)	0.02	0.02
	MeOH (0.1)	0.09	0.54
	C_6F_5OH (0.1)	0.65	1.54
DMSO (0.1)	none	0.11	0.26
	THF (0.1)	0.19	0.25
	THF (0.5)	0.10	0.24
	benzene (0.1)	0.05	0.14
	benzene (0.5)	0.10	0.10
	MeOH (0.1)	0.11	0.37
	MeOH (0.5)	0.30	0.31
	C_6F_5OH (0.1)	0.28	0.38
	C_6F_5OH (0.5)	0.35	0.45
MeCN (0.1)	none	0.09	0.13
	DMSO (0.1)	0.07	0.18
	DMSO (0.5)	0.05	0.08

[a] Conditions: 20 bar CO_2, 20 bar H_2, 5 mmol NEt_3, 3 μmol $RuCl(O_2CMe)(PMe_3)_4$, 50 °C. Yield expressed as mol formic acid per mol NEt_3.

Using two of these additives simultaneously allowed for some interesting comparisons (Table 6). Using both DMSO and an alcohol was less effective than using the alcohol alone but more effective than using DMSO alone. In other words, the presence of DMSO weakened the beneficial effects of added acidic alcohol. Using DMSO and another nonprotic additive (e.g., MeCN, benzene, or THF) together was less effective than using DMSO alone.

Methyl Carbonate Salts. Alcohols react with CO_2 to form the alkylcarbonic hemi-acid,[59] particularly in the presence of tertiary amine bases (eq 2).[18] The methyl carbonate salt of DBU can be isolated as a stable white solid by bubbling CO_2 through a THF solution containing equal amounts of methanol and DBU. In contrast, the NEt_3 methyl carbonate salt can be observed using high-pressure in situ NMR and IR spectroscopies, but the salt decomposes back to CO_2 and methanol without an overpressure of CO_2. The white DBU methyl carbonate salt shows ^{13}C NMR resonances at 48.7 and 160.5 ppm for the methyl and ester carbons, respectively, and an IR band for the C═O ester stretch at 1654 cm^{-1}. In situ spectroscopy of the NEt_3 salt shows ^{13}C NMR resonances at 52.3 and 160.1 ppm and an IR band at 1642 cm^{-1}.

$$CO_2 + MeOH + B \xrightarrow[MeOH\ or\ THF]{} Me\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- \cdot HB^+ \qquad (2)$$

The alkyl carbonate ammonium salts can be formed from most alkyl alcohols but only in polar solvents. The formation of the alkyl carbonate salts is instantaneous upon mixing and with NEt_3 is completely reversible. Under 20 bar of CO_2, a 2 M NEt_3 solution in methanol gives an 85% yield (based on NEt_3) of the methyl carbonate salt (determined by ^{13}C NMR). No methyl carbonate could be observed by ^{13}C NMR under 20 bar CO_2 with a 2:1 NEt_3:MeOH solution. However, IR being more sensitive for methyl carbonate than NMR does show a small band at 1650 cm^{-1} demonstrating that methyl carbonate is formed even under amine-rich conditions. The amount of methyl carbonate produced in the catalytic systems ranges from very high (>50% of the amine concentration) for methanol-rich solutions and lower than 3% for amine-rich solutions.[18] Phenol and substituted phenols did not form aryl carbonates even under high pressures of CO_2 presumably because of the more acidic proton when compared to alkyl alcohols. The alkyl carbonate salts are extremely sensitive to small amounts of acid. The methyl carbonate DBU salt decomposed when exposed to phenol.

The possibility that the mechanism of CO_2 hydrogenation may involve direct hydrogenation of methyl carbonate was explored by testing the ability of the Ru catalyst to hydrogenate solutions of the DBU salt of methycarbonic acid (eq 3). The [DBUH]-[OC(O)OMe] salt (5 mmol) and $RuCl(O_2CMe)(PMe_3)_4$ catalyst precursor (3 μmol), in MeOH solution (0.1 or 10 mmol MeOH), were exposed to 20 bar H_2 for 9 h at 50 °C. No formic acid was produced. Even when extra DBU was added, no formic acid production was observed. However, when a small amount of CO_2 was added, a small amount of formic acid was formed (0.065 mol per mole of DBU).[60] In contrast, the hydrogenation of CO_2 in DBU/MeOH mixtures is extremely rapid under similar conditions (0.92 mol formic acid per mol DBU after 1 h). This is strong evidence that hydrogenation of the methyl carbonate anion by the Ru catalyst is not the mechanistic path by which CO_2 is hydrogenated.

$$Me-O-\overset{\overset{O}{\|}}{C}-O^- \cdot HDBU^+ + H_2 \xrightarrow[MeOH,\ 50°C,\ 9\ h]{RuCl(OAc)(PMe_3)_4} \text{no formic acid} \qquad (3)$$

In Situ NMR Spectroscopy. Preliminary in situ ^1H and $^{31}P\{^1H\}$ NMR spectroscopic studies of the catalytic reaction to produce formate using $RuCl(OAc)(PMe_3)_4$ were performed. In general, little information about the catalyst structure can be gained using ^1H NMR spectroscopy because of our use of nondeuterated solvents, NEt_3 and MeOH. However, we can observe the growth of formate during the reaction by ^1H NMR spectroscopy. We do not observe any hydride resonances in the ^1H NMR spectrum even though they appear to be present as observed by ^{31}P NMR spectroscopy. This is presumably due to proton exchange between the metal center and alcohol, methylcarbonic acid, H_2, or protonated amine which are all present in the reaction mixture. We also observed this phenomenon with a catalyst system generated in situ from $[RuCl_2(C_6H_6)]_2$ and dppm.[61]

The in situ ^{31}P NMR spectroscopy does yield important information about the metal center before and during the reaction. The initial ^{31}P NMR spectrum of $RuCl(OAc)(PMe_3)_4$ dissolved in $CDCl_3$ shows the expected A_2BC splitting pattern with 1:1:2 integrations for the multiplets at 14.3, 11.2 ppm and the psuedo triplet at −6.2 ppm for the cis isomer. A small set of two triplets at 22.2 and −1.0 ppm, which integrate 1:1, and a set of broad peaks centered at 28 ppm are also observed. The two triplets are most likely due to $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ while the broad signals are due to an impurity or species in exchange on the NMR time scale. At least one of these species, near 28 ppm, has been identified as the triphosphine, *fac*-$RuCl(\eta^2\text{-}OAc)$-

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(60) ^{13}C-labeling of the methyl carbonate to determine the source of the C in the formic acid product was not successful because of rapid exchange between free $^{12}CO_2$ and the labeled $[DBUH][O^{13}C(O)OMe]$.

(61) Tai, C. C.; Pitts, J.; Main, A. D.; Linehan, J.; Munshi, P.; Jessop, P. G. *Inorg. Chem.* **2002**, *41*, 1606−1614.

$(PMe_3)_3$.[62] These equilibria of $RuCl(OAc)(PMe_3)_4$ with other species in solution make the subsequent structural determinations under catalytic conditions difficult.

Adding methanol to the $CDCl_3$ solution described above changes and simplifies the ^{31}P NMR spectrum. The characteristic 1:1:2 multiplet:multiplet:triplet of the *cis*-$RuCl(OAc)(PMe_3)_4$ and the broad features at 28 ppm dissappear completely upon addition of enough methanol to constitute 7% of the solution (40 equivalents based on *cis*-$RuCl(OAc)(PMe_3)_4$). The major signals are the two previously observed triplets (A_2B_2 pattern) at 21.9 and −1.5 ppm which integrate 1:1, $^2J_{p-p} = 30.2$ Hz. There is also a very small doublet at 24.0 ppm and a triplet at 20.5 ppm which integrate 2:1, $^2J_{P-P} = 42.9$ Hz. This latter species can be reproduced by addition of methanol to a $CDCl_3$ solution of authentic *fac*-$RuCl(\eta^2\text{-}OAc)(PMe_3)_3$.[62] The structure of this species is now under investigation.

When solid *cis*-$RuCl(OAc)(PMe_3)_4$ is dissolved in MeOH/NEt_3 (3:1 molar ratio), the major species by $^{31}P\{^1H\}$ NMR is the same set of two triplets seen in $CDCl_3$/MeOH for $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$. Minor features are the broad features at 28 ppm observed in $CDCl_3$ and the multiplets due to *cis*-$RuCl(OAc)(PMe_3)_4$. Immediate formation of new trans and cis oriented complexes, of the form *cis*-$Ru(X)(Y)(PMe_3)_4$, *trans*-$Ru(X)(Y)(PMe_3)_4$, or *trans*-$Ru(X)_2(PMe_3)_4$, was apparent upon pressurization to 20 bar with H_2 at room temperature. The poor resolution of the new multiplets due to cis compounds and their rapid transformations did not allow us to distinguish the coupling patterns, and no identification of the new cis species was possible. The trans species at −3.9 ppm was most likely *trans*-$Ru(H)(X)(PMe_3)_4$ (X = Cl or OCH_3) or *trans*-$Ru(H)_2(PMe_3)_4$. A large amount of $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ was present in this reaction mixture, but *cis*-$RuCl(OAc)(PMe_3)_4$ was immediately consumed. Upon heating the mixture to 50 °C, the known[17] *cis*-$RuH_2(PMe_3)_4$ (A_2B_2 pattern at 1.7 and −6.5 ppm) and *cis*-$RuHCl(PMe_3)_4$ (A_2BC pattern at −4, −16.5, and 19.8 ppm) are seen to grow in as the resonances for $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ disappear.

The $^{31}P\{^1H\}$ NMR of this reaction mixture immediately after pressurization with CO_2 (20 bar) showed a rapidly changing spectrum. Initially the cis dihydride and cis hydridochloride species are present but over several hours the resonances for these species disappear. The trans resonance at −3.9 ppm remains throughout the reaction. New resonances for at least two new cis products and one trans product are observed but were not identified. After several hours, the NMR spectrum of this reaction mixture is relatively clean with only five species observed. The three new sets of resonances which predominate the spectrum correspond to the known *cis*-$RuH(O_2CH)(PMe_3)_4$ (A_2BC pattern at −0.3, −11.8, and 19.8 ppm)[3] and the unknown *cis*-$Ru(O_2CH)_2(PMe_3)_4$ (A_2B_2 pattern at 0.6 and −6.3 ppm) and *trans*-$Ru(O_2CH)_2(PMe_3)_4$ (singlet at −4.2 ppm). The assignments of the diformato species are made on the basis of the known formato species observed for the CO_2 insertion into the Ru−H bond in $Ru(H)_2(dmpe)_4$ and those observed for Ru(X)(Y)$(dppm)_2$ systems.[61,63] The fourth species is represented by the singlet at −3.9 ppm and the fifth species is represented by the broad resonances centered at 28 ppm. Both of these features are observed throughout the reaction. Depressurization of the NMR cell followed by extraction with $CDCl_3$ in air yielded $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ as the major ruthenium-containing product. The ruthenium-formato and the ruthenium-hydride species do not appear to be air-stable.

These in situ NMR results show that this system is more complicated than the Ru-dppm system previously studied.[61] The PMe_3 ligands impart more lability than does the dppm chelating ligand as shown by the consistent appearance throughout the experiments of the broad features at 28 ppm. In dppm, there is no broad feature observed in the ^{31}P NMR under any conditions. The dppm ligand also forms the dihydride and the hydridochloride exclusively in the trans geometry whereas the PMe_3 ligand forms both trans and cis in approximately equal amounts. The formato complexes are formed as both cis and trans isomers with both ligands.

These NMR results show that the catalyst system involving ruthenium phosphines is complicated. The presence of the $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ salt in the initial methanol-containing solution may be important in the subsequent catalytic activity. Preliminary titrations of $CDCl_3$ solutions containing *cis*-$RuCl(OAc)(PMe_3)_4$ with various alcohols show that the conversion to $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ followed the trend *o*-cresol ≥ MeOH > EtOH > IPA > *t*-BuOH. Methanol and *o*-cresol yielded 100% of $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ with 25% (by volume) addition and addition of *tert*-butyl alcohol resulted in no conversion to $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$. This is similar to the order of reactivity observed for the conversion of CO_2 to formate. Under the initial catalytic reaction conditions used in this paper, the major ruthenium-containing species present before addition of H_2 would be $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ for the more active alcohols.

Discussion

Can Acidic Alcohols Protonate Amines? Although acid/base behavior is usually described in terms of aqueous-scale pK_a's of the reactants, that scale may not be appropriate for reactions in nonaqueous media. If the hydrogenation of CO_2 is performed in liquid NEt_3, in supercritical CO_2, or in any other nonpolar aprotic solvent, then the acid/base behavior of the reagents and products is best approximated by a nonaqueous scale of pK_a values. Of course, pK_a scales for acids in NEt_3 or $scCO_2$ are unavailable; the closest available scale may be that in THF.[40] In a nonpolar aprotic solvent, ionic species are destabilized and therefore neutral acids such as alcohols and carboxylic acids have greatly decreased acidity (greatly raised pK_a's) while cationic acids such as $HNEt_3^+$ retain their acidity. To illustrate this, the aqueous, DMSO, and THF scale pK_a's of the alcohols and amines are compared in Tables 3 and 5. In the aprotic solvents, phenols have pK_a's much higher than that of $HNEt_3^+$ and would therefore not necessarily be deprotonated by NEt_3 in nonpolar solvents.

Alcohols and triethylamine in nonpolar solvents are known to form 1:1 hydrogen-bonded adducts ArOH···B which are in equilibrium with the proton-transferred species (eq 4).[64,65] The position of the proton-transfer equilibrium depends on the relative acidities of the phenol and the protonated amine and

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(63) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *15*, 5166−5169.
(64) Albrecht, G.; Zundel, G. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 553−561.
(65) Krämer, R.; Zundel, G. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 301−305.

the solvent. Ratajczak and Sobczyk[66] showed that in benzene solution, phenols having aqueous-scale pK_a's below 4 will be essentially completely deprotonated by NEt_3, while those with pK_a's above 8 will form only the hydrogen-bonded adduct. Baba et al.[67] reported that *p*-nitrophenol (pK_a 7.15),[54] for example, would exist as an adduct with NEt_3 in the nonpolar solvent isooctane, while in 1,2-dichloroethane the solution would contain a roughly equimolar mixture of the adduct and the proton-transferred species. In acetonitrile, NEt_3 and *p*-nitrophenol exist as a solvent-separated ion pair. Zundel[65] showed that the degree of proton transfer for a mixture of NEt_3 and 2,4,6-trichlorophenol (pK_a 6.2)[68] is 10% in heptane and 12% in CCl_4 at 30 °C.

$$\mathrm{ArOH} + \mathrm{B} \rightarrow \mathrm{ArOH\cdots B} \overset{\text{proton transfer}}{\rightleftharpoons} \mathrm{ArO^-\cdots HB^+} \rightleftharpoons \mathrm{ArO^-} + \mathrm{HB^+} \quad (4)$$

The acidic phenols are not able to protonate pyridine in nonpolar solvents. The ΔpK_a (i.e., pK_a(pyridinium)−pK_a(ROH)) required for the partial protonation of pyridines by a phenol in CCl_4 is 1.6 for partial protonation and 5 for essentially complete protonation, so that a phenol with a pK_a below 3.6 is required to at least partially protonate pyridine itself.[64,69] None of the acidic alcohols used in the present study had a pK_a that low. Even formic acid is not sufficiently acidic to protonate pyridine.[70] This is likely the reason for the low yield of formic acid when any alcohol/pyridine combination was used.

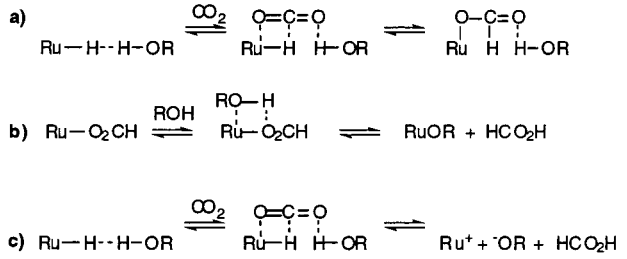
The reaction solution at the start of the experiments in triethylamine or similar liquid amines is nearly as nonpolar as heptane. Therefore, we can expect that only the most acidic phenols (C_6F_5OH, C_6Cl_5OH, and 2,4-$(O_2N)_2C_6H_3OH$) will substantially protonate triethylamine in the reaction solution. However, the acid/base equilibria between acidic alcohols and the amines should change as the hydrogenation proceeds. As formic acid accumulates, the reaction medium changes from nonpolar aprotic to polar protic so that ion pairs and even solvent-separated free ions are stabilized and the pK_a values of the acids approach aqueous scale values rather than THF-scale values. At this time, the acids present (alkylcarbonic acids, formic acid, and most of the acidic alcohols) will be acidic enough to protonate triethylamine. Thus, charged species such as RO^-, $ROC(O)O^-$, and HNR_3^+ may be less stable and therefore at lower concentrations during the early stages of the reaction but would increase in stability and concentration as the reaction proceeds.

With some nonpolar solvents (including $scCO_2$), the formic acid/triethylamine adduct forms a second liquid phase rather than remain in solution in the nonpolar solvent.

The acid/base behavior described above would be quite different, of course, if the CO_2 hydrogenation were performed in a highly polar or protic solvent such as DMSO or methanol.

The Role of the Alcohol. The in situ spectroscopic experiments suggest that the alcohol helps to convert much of the catalyst precursor to $[Ru(OAc)(PMe_3)_4]Cl$. However, if that is the only role of the alcohol, then methanol should be as effective as the acidic phenols. The superiority of the latter in promoting the hydrogenation indicates that the alcohol has another role to play. This other role of the alcohol is still unknown, although the new data offer some hints. We have already concluded that the alcohol is not serving simply as a solvent modifier because only trace quantities of alcohol are needed, too small to have a significant effect on the physical properties of the reaction medium.[14] A chemical effect of the alcohol on the reaction mechanism is far more likely. Because the alcohol is used in the presence of CO_2 and base, the alcohol may not be involved directly in the mechanism but rather it may be converted by reaction with CO_2, amine, or both to other species that may be involved in the mechanism. These other species could include HNR_3^+, RO^-, ROC(O)OH, or $ROC(O)O^-$. The possible roles of each of these species will be discussed in turn.

Scheme 1. Three Mechanisms by Which an Acidic Alcohol Could Assist in the Hydrogenation of CO_2. In These Mechanisms, the Alcohol Could Be Initially Ru-Bound or Hydrogen-Bonded to the Complex



(a) Alcohol/Alkoxide. Alcohol could be involved in the mechanism in several ways (Scheme 1), but without firmer knowledge of the mechanism of the hydrogenation, it is difficult to narrow down the possibilities. Alcohol could assist in the insertion of CO_2 into the Ru−H bond (Scheme 1a),[6,15] it could donate a proton to a formate ligand as the second step in an ionic hydrogenation (Scheme 1b), it could donate a proton to the CO_2 in a concerted ionic hydrogenation mechanism (Scheme 1c)[15,71] as suggested by Noyori for the hydrogenation of ketones,[72,73] or it could combine with trialkylamine to reduce the metal complex.[74,75] These possibilities do not require an inner-sphere alcohol ligand; the alcohol could be hydrogen-bonded to the formate or hydride[13,76] ligands. All of these possibilities are likely to be more efficient with a highly acidic alcohol, as long as the alcohol is not so acidic that it is completely dissociated in the amine solution.

(b) Protonated Amine. The role of HNR_3^+, if it is involved in the mechanism, could be similar to the possible roles of ROH: assisting in CO_2 insertion into Ru−H (cf. Scheme 1a) or acting as the proton source in a Noyori-type mechanism (cf. Scheme 1c).[13] The latter possibility was suggested by Matsubara[13] for the complex $[(C_5H_4(CH_2)_2NHMe_2^+)RuH(dppm)]BF_4$. That complex contained a dangling amine, which when protonated was well placed to donate its proton to a CO_2 molecule

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(70) Lindemann, R.; Zundel, G. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 979−990.
(71) As far as we are aware, the first suggestion of a concerted ionic hydrogenation mechanism for CO_2 hydrogenation was made by Pomelli et al. for the reaction catalyzed by Rh phosphine complexes, but in their mechanism coordinated formic acid was the proton donor: Pomelli, C. S.; Tomasi, J.; Sola, M. *Organometallics* **1998**, *17*, 3164−3168.
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(73) See also the work of Morris: Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 2655−2657.
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in concert with hydride transfer. Surprisingly, however, the complex had extremely low catalytic activity (Table 1).

However, the results in the present system indicate that the alcohols are not acting as simply a proton source for the generation of protonated amine; this was shown by the ineffectiveness of 2,6-di(*tert*-butyl)phenol, which is more acidic than methanol. Also, one would expect formic acid to be even more effective than alcohols at protonating triethylamine; thus after a small amount of conversion, protonated amine would be abundantly available regardless of the initial choice of alcohol. There is no evidence that formic acid is autocatalytic. The results therefore are inconsistent with the role of the alcohol being the protonation of the amine.

(c) Alkylcarbonic Acid/Alkyl Carbonate Anion. Although the pK_a of methylcarbonic acid in nonpolar solvents is not known, it is likely to be higher than that of $HNEt_3^+$. It therefore seems uncertain that the species ROC(O)OH would be deprotonated to any significant extent by triethylamine in experiments performed in liquid NEt_3 or supercritical CO_2. Without deprotonation, the thermodynamic driving force for the reaction between CO_2 and ROH is decreased. This explains the nondetection by IR of alkyl carbonate/alkylcarbonic acid when CO_2 is bubbled into MeOH/NEt_3 mixtures which are predominantly NEt_3. However, as the hydrogenation of CO_2 continues, and formic acid accumulates, the reaction medium changes from nonpolar aprotic to polar protic, so that the pK_a values of the acids and bases present more closely match aqueous scale values. At this point, the alkylcarbonic acid will be acidic enough to protonate triethylamine. Thus, the stability and concentration of methylcarbonic acid should increase during the reaction. This was confirmed by in situ IR experiments, in which the small 1650 cm^{-1} band for methyl carbonate anion increased in intensity as the amount of formic acid increased until the point when formic acid had protonated most of the amine; the methyl carbonate peak then declined in intensity and then disappeared.

Because in situ IR experiments show that alkyl carbonate anion exists in the reaction solution during CO_2 hydrogenation, it is possible that the hydrogenation of formic acid proceeds by Ru-catalyzed hydrogenation of the alkyl carbonate. However, the failure of attempts to directly hydrogenate [DBU·H^+][$^-$OC(O)OMe] using $RuCl(OAc)(PMe_3)_4$ as the catalyst precursor shows that carbonate hydrogenation is not facile. Therefore, carbonate formation, to the extent that it occurs, is a side reaction which ties up alcohol, base, and CO_2 and thereby interferes with the hydrogenation.

Conclusions

Selection of the appropriate amine and alcohol has allowed a large increase in the rate of hydrogenation of CO_2 catalyzed by the complex $RuCl(O_2CMe)(PMe_3)_4$. In particular, it is important to use either triflic acid or a highly acidic alcohol, preferably one that has an aqueous-scale pK_a below that of the protonated amine. For example, using pentafluorophenol as the alcohol and triethylamine as the base in supercritical CO_2 gave a turnover frequency for formic acid production of 95 000 h^{-1}, more than an order of magnitude greater than previously observed. Even higher rates of reaction would be likely in the presence of triflic acid and DBU, but the rates would surpass our ability to measure them. The alcohol has been shown, by in situ NMR spectroscopy, to induce the Ru-containing catalyst precursor to transform into a cationic complex. The alcohol is not likely to generate carbonic acids or protonated amines in solution, but the alcohol could be involved as either a hydrogen-bond donor or a proton donor in a concerted ionic hydrogenation mechanism.

High-pressure spectroscopic studies will be continued to elucidate the mechanism and the role of the acidic alcohols in this reaction.

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