## Hydrogenation of carbon dioxide in the presence of rhodium catalysts

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The results of  $CO_2$  hydrogenation in the presence of the Wilkinson complexes, *viz.*, RhCl<sub>3</sub> and acacRh(CO)<sub>2</sub>, at room temperature and excess PPh<sub>3</sub> are presented. The influence of different ions on the catalytic properties of the Rh complexes was studied. Methanol and methyl formate are formed along with formic acid in the presence of an inorganic salt. Ions that are the most active in the formation of formic acid are the least active in methanol formation.

Key words: hydrogenation, carbon dioxide, formic acid, methanol, triphenylphosphine.

It has previously<sup>1</sup> been established that carbon dioxide undergoes a rapid hydrogenation to formic acid in the presence of the Wilkinson complex with excess PPh<sub>2</sub> at room temperature and low pressures. Hydride rhodium complexes were found to be catalytically active species in this reaction. The deactivation of RhCl(PPh<sub>3</sub>)<sub>3</sub> is caused by the elimination of triphenylphosphine from the coordination sphere. This process is suppressed when the reaction occurs in excess PPh<sub>3</sub> or in the presence of HCl and KNO<sub>3</sub>.<sup>2</sup> To get further insight into the nature of catalytically active complexes and to find methods for their stabilization, it seemed of interest to study the influence of various additives on the catalytic properties of the Wilkinson complex in this reaction. In this work, we report on the results of studying the influence of the nature of inorganic salts on stability of the Wilkinson complex in carbon dioxide hydrogenation to formic acid. The effect of different phosphorus-containing additives on the selectivity of the process is also discussed.

## Experimental

Hydrogenation of carbon dioxide was conducted in a stainless steel autoclave (150 mL) with an electromagnetic stirrer. Before the reaction, the rhodium complexes ([Rh] =  $10^{-2}$  g-at L<sup>-1</sup>) and additives used (PPh<sub>3</sub>, inorganic salts, methanol) were stirred in a mixture consisting of dimethyl sulfoxide (DMSO) and triethylamine (NEt<sub>3</sub>) under H<sub>2</sub>. After this, CO<sub>2</sub> (4 MPa) was introduced into the reactor following by hydrogen to bring the pressure in the reactor to 6 MPa. This moment was considered to be the onset of the reaction. The reaction was carried out at 25 °C for 22 h. The liquid product was sampled during hydro-

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genation. Formic acid was detected by <sup>1</sup>H NMR. The concentration of formic acid obtained as an adduct HCOOH • NEt<sub>3</sub> was calculated from the amount of amine used. The content of methanol and methyl formate was determined by GLC on a Chrom-5 chromatograph (capillary column 50 m, phase PEG20M, flame-ionization detector, carrier gas nitrogen, 80 °C). Dimethylformamide was used as an internal standard. The concentration of introduced salts was  $10^{-2}$  mol L<sup>-1</sup>. In experiments with variable molar ratio of NEt<sub>3</sub> to methanol, the overall concentration of methanol and triethylamine was kept constant and taken on the basis of the NEt<sub>3</sub> concentration usually used in this reaction.

Complexes  $RhCl(PPh_3)_3^3$  and  $acacRh(CO)_2^4$  and ligand ethriolphosphite (ETPO)<sup>5</sup> were synthesized according to known procedures. Commercially available (Fluka)  $RhCl_3$ ,  $PPh_3$ , and DMSO were used as received. Triethylamine was distilled before use.

## **Results and Discussion**

As shown previously,<sup>2</sup> the hydrogenation of CO<sub>2</sub> to formic acid in the presence of the Wilkinson complex with an additive of KNO<sub>3</sub> occurs with a higher rate than that with HCl addition. Therefore, the influence of different cations of nitrate salts on the catalytic properties of the Wilkinson complex was studied. The replacement of K<sup>+</sup> by lithuim cations decreases the reaction rate (Fig. 1). However, in the presence of Li<sup>+</sup>, the yield of formic acid after 22 h is higher than that in the case of the Wilkinson complex without salt additives. In the presence of ammonium nitrate, the reaction rate is low, and after 22 h the reaction still proceeds. In the case of Cr<sup>3+</sup> and Al<sup>3+</sup> ions, an induction period appears; however, the reaction rate increases sharply after 16 h. Thus, in all cases, the addition of salts results in the stabilization of catalyti-

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**Fig. 1.** Influence of cations of nitrate salts on the yield of formic acid in the presence of the RhCl(PPh<sub>3</sub>)<sub>3</sub> +3PPh<sub>3</sub> catalytic system: *1*, KNO<sub>3</sub>; *2*, without addition of salts; *3*, LiNO<sub>3</sub>; *4*, Al(NO<sub>3</sub>)<sub>3</sub>; *5*, Cr(NO<sub>3</sub>)<sub>3</sub>; *6*, NH<sub>4</sub>NO<sub>3</sub>.

cally active complexes, and the reaction rate increases significantly only in the case of KNO<sub>3</sub>.

In the presence of salts, methanol and methyl formate are formed along with formic acid (Table 1). The highest yield of formic acid was obtained when using  $K^+$  and  $Li^+$ , whereas the highest yield of methanol is achieved in the presence of  $Al^+$  and  $Cr^+$ . Based on their activity in formic acid formation, the cations can be arranged in the following series (see Table 1):

 $K^+ > Li^+ > Al^{3+} \approx Cr^{3+} > NH_4^+,$ 

while for the formation of methanol the series is

 $Cr^{3+} > Al^{3+} > Li^+ > K^+ > NH_4^+.$ 

It can be concluded that cations that are the most active in formic acid formation are the least active in the formation of methanol.

Table 1. Influence of the nature of the cation on the catalytic properties of the  $RhCl(PPh_3)_3+3PPh_3$  system in  $CO_2$  hydrogenation

Salt	[HCOOH]	[MeOH]	[MF]*	
	mol L <sup>-1</sup>			
_	0.950	_	_	
KNO3	1.250	0.025	0.010	
LiNO <sub>3</sub>	0.970	0.045	0.020	
$Al(NO_3)_3$	0.640	0.092	0.026	
$Cr(NO_3)_3$	0.640	0.124	0.010	
NH <sub>4</sub> NO <sub>3</sub>	0.520	0.006	0.004	

\* MF is methyl formate.

**Table 2.** Influence of the nature of the anion on the catalytic activity of the RhCl(PPh<sub>3</sub>)<sub>3</sub>+3PPh<sub>3</sub> system in CO<sub>2</sub> hydrogenation

Salt	[HCOOH]	[MeOH]	[MF]			
		$mol L^{-1}$				
_	0.950	_	_			
KI	0.950	0.040	0.020			
KNO3	1.250	0.025	0.010			
$K_2SO_4$	0.530	0.015	0.005			
$K_2CO_3$	0.690	0.010	0.008			
K <sub>3</sub> PO <sub>4</sub>	0.800	0.039	0.010			

The nature of anions also exerts a significant effect on the formation of formic acid and methanol (Table 2). In the presence of potassium nitrate, the yield of formic acid increased. Phosphate and iodide anions do not virtually affect the formation of formic acid, but methanol is also formed in their presence. The addition of sulfate and carbonate ions decreases the yield of formic acid. At the same time, the yield of methanol increases in the presence of these salts. The order of decreasing activity in formic acid formation for anions is

$$NO_3^- > I^- > PO_4^{3-} > CO_3^{2-} \ge SO_4^{2-}$$

In the case of methanol formation, the order of decreasing activity is

$$I^- > NO_3^- > PO_4^{3-} > SO_4^{2-} \ge CO_3^{2-}$$

The formation of methanol at room temperature is an unusual result because, as known,<sup>6,7</sup> high pressures and elevated temperatures are needed to form methanol from carbon dioxide. To explore the possibility of increasing the methanol yield and to get insight into the nature of an active site, we studied the influence of different ligands on the yield of methanol in the presence of various rhodium precursors of the catalyst of  $CO_2$  hydrogenation (Table 3).

In the case of RhCl<sub>3</sub> modified with PPh<sub>3</sub>, only formic acid is formed. When salt KNO3 is added, the yield of formic acid decreases, and methanol and methyl formate are formed. If the reaction is carried out without triphenylphosphine in the presence of KNO<sub>3</sub> only, no formic acid is formed, and the yield of methanol increases significantly. The highest yield of methanol is achieved when the reaction is carried out in the presence of RhCl<sub>3</sub> and OPPh<sub>3</sub>, and no formic acid is formed in this case. When  $acacRh(CO)_2$  was used, the highest yield of methanol was obtained on unmodified  $acacRh(CO)_2$  in the presence of KNO<sub>3</sub>. Nearly no methanol forms in the absence of NEt<sub>3</sub>. Interesting results were obtained when ethriolphosphite with an enhanced withdrawing power was used. Unlike PPh<sub>3</sub>, the modification of acacRh(CO)<sub>2</sub> with ETPO does not result in the formation of formic acid but

Ligand	[HCOOH]	[MeOH]	[MF]				
(P/Rh = 6)	mol L <sup>-1</sup>						
	RhCl <sub>3</sub>						
PPh3*	0.500	_	_				
PPh <sub>3</sub>	0.390	0.004	0.002				
Without ligand	_	0.040	0.001				
OPPh <sub>3</sub> *	_	0.210	0.003				
acacRh(CO) <sub>2</sub>							
PPh3*	0.500	_	_				
PPh3**	0.420	0.004	0.002				
Without ligand	—	0.457	0.014				
Without ligand	—	Traces	—				
OPPh <sub>3</sub> *	—	0.032	Traces				
ETPO	—	0.064	0.002				
ETPO*	—	0.177	0.158				
RhCl(PPh <sub>3</sub> ) <sub>3</sub>							
PPh <sub>3</sub> *	0.950	—	—				
PPh <sub>3</sub>	1.250	0.025	0.010				
OPPh <sub>3</sub>	—	0.155	0.015				
OPPh <sub>3</sub>	—	0.030	Traces				

**Table 3.** Hydrogenation of  $CO_2$  in the presence of the rhodium catalysts

\* In the absence of KNO<sub>3</sub>.

\*\* In the absence of NEt<sub>3</sub>.

a large amount of methanol is formed. The yield of methanol decreases sharply when  $KNO_3$  is added. For the Wilkinson complex, the highest yield of methanol was obtained in the presence of  $KNO_3$  and  $OPPh_3$ .

For the catalytic system of  $RhCl_3$  and  $OPPh_3$ , the replacement of  $KNO_3$  by other salts decreases the yield of methanol (Table 4). Similar results were obtained for  $acacRh(CO)_2$ .

The presence of a salt in the reaction medium stabilizes a catalytically active complex to form methanol and methyl formate. As a rule, salts that manifest activity in the formation of formic acid are inactive in the formation of methanol. A necessary condition for the formation of HCOOH is the presence of PPh<sub>3</sub> in the reaction medium, while the presence of PPh<sub>3</sub> is not necessary for methanol

**Table 4.** Hydrogenation  $CO_2$  to formic acid in the presence of different salts

Compound	Ligand $(P/Rh = 6)$	Additive	[MeOH]	[MF]
			mol	$L^{-1}$
RhCl <sub>3</sub>	OPPh <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>	0.008	0.002
5	OPPh <sub>3</sub>	K <sub>2</sub> ČO <sub>3</sub>	0.007	_
	OPPh <sub>3</sub>	ĸĨ	0.002	0011
	_	$K_2CO_3$	0.030	0.016
$acacRh(CO)_{2}$	_	KĪ	0.070	_
	_	$K_2CO_3$	0.030	0.016
	OPPh <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>	0.012	0.014

formation. The presence of triethylamine in the reaction medium is needed for the formation of both formic acid and methanol.

Evidently, methanol and formic acid form on different catalytically active sites. The influence of ions on their stability is selective; however, the presence of a salt in the reaction medium exerts a stabilizing effect on the formation of both formic acid and methanol.

Methyl formate can form through the esterification of formic acid with methanol. To reveal the role of methanol in the hydrogenation of  $CO_2$ , we studied the influence of the  $CH_3OH$  concentration on the distribution of the reaction products. The addition of a minor amount of methanol instead of DMSO insignificantly increases the yield of formic acid and sharply increases the yield of methyl formate (Fig. 2, *a*). However, the further increase



**Fig. 2.** Plots of the concentrations of formic acid and methanol *vs.* molar ratios  $CH_3OH : DMSO(a)$  and  $NH_3 : CH_3OH(b)$  in  $CO_2$  hydrogenation in the presence of the catalytic system RhCl(PPh<sub>3</sub>)<sub>3</sub>+3PPh<sub>3</sub>: *1*, HCOOH; *2*, methyl formate.

in the methanol concentration results in an increase in the yield of formic acid and a decrease in the yield of methyl formate. The decrease in the methyl formate yield is apparently related to the fact that esterification is not the only way to form methyl formate under the conditions of  $CO_2$  hydrogenation. The highest yield of the acid is achieved at the ratio MeOH : DMSO = 6.8. Thus, methanol is an esterifying agent and also promotes the hydrogenation of  $CO_2$  to formic acid. The hydrogenation of  $CO_2$ is thermodynamically unfavorable and can occur in a high yield only in the presence of tertiary amines.<sup>8</sup> Methanol binds formic acid to form methyl formate and thus initiates  $CO_2$  hydrogenation in the same manner as NEt<sub>3</sub>.

The influence of the NEt<sub>3</sub> : MeOH ratio on the yield of reaction products was studied. An increase in the NEt<sub>3</sub> to methanol molar ratio to 0.15 (see Fig. 2, *c*) increases the yield of all reaction products; however, the further increase in this ratio decreases the yields of both formic acid and methyl formate. Carbon dioxide is not hydrogenated without NEt<sub>3</sub> in the presence of DMSO as a solvent (Table 3), and neither formic acid, nor methyl formate were found in the reaction products. The partial replacement of NEt<sub>3</sub> by methanol considerably decreases the yield of formic acid. Thus, under conditions of  $CO_2$  hydrogenation, formic acid can form in a high yield in the presence of  $NEt_3$  only, which is a component of a catalytically active complex.

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