

# Hydrogenation of CO<sub>2</sub> to formic acid in the presence of the Wilkinson complex

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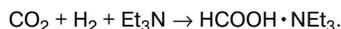
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Formic acid was synthesized in a high yield at room temperature in the presence of the Wilkinson complex and an excess of PPh<sub>3</sub>. The catalytic properties of the rhodium complex depend strongly on the reaction conditions. The mechanism of the rhodium catalyst deactivation was studied by the kinetic method and <sup>31</sup>P NMR spectroscopy. The methods for the stabilization of the rhodium catalyst were found.

**Key words:** hydrogenation, carbon dioxide, formic acid, Wilkinson complex, triphenylphosphine, <sup>31</sup>P NMR spectroscopy.

Hydrogenation to formic acid is an attractive method for CO<sub>2</sub> fixation because only 1 mole of H<sub>2</sub> is needed for the formation of formic acid and the reaction occurs without oxygen loss to CO<sub>2</sub>. The process is thermodynamically unfavorable<sup>1</sup> but can result in a high yield in the presence of tertiary amines binding the acid



Two main approaches to this reaction are presently known. Formic acid is obtained under supercritical conditions in the presence of the ruthenium complexes.<sup>2</sup> In solutions of the rhodium complexes modified by the R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub> bidentate phosphine ligands, the process is carried out at room temperature and a low pressure.<sup>3</sup> This is precisely the direction of studies which presently seems most promising from the viewpoint of utilization of carbon dioxide and a decrease in its emission. In this work, the results of studying CO<sub>2</sub> hydrogenation in the presence of the Wilkinson complex (RhCl(PPh<sub>3</sub>)<sub>3</sub>) are presented. The conditions under which the reaction occurs with a high yield were found, and the routes of possible deactivation of catalytically active complexes were studied.

## Experimental

The hydrogenation of CO<sub>2</sub> was carried out at 25 °C in a stainless steel autoclave (150 mL) with an electromagnetic stirrer. Before the reaction, the rhodium complex with the ligands was dissolved upon stirring in a solvent—NEt<sub>3</sub> mixture in an

atmosphere of one of the following gases: air, argon, CO<sub>2</sub>, or H<sub>2</sub>. Then H<sub>2</sub> and CO<sub>2</sub> were consecutively introduced into the reactor until a specific pressure was achieved. This moment was considered as the beginning of the reaction. Samples of the liquid product, which was spectroscopically analyzed, were taken during the reaction. Formic acid was detected by <sup>1</sup>H NMR spectroscopy, and products of transformation of triphenylphosphine and triphenylphosphine-rhodium complexes were detected by <sup>31</sup>P NMR spectroscopy. Dimethylformamide (<sup>1</sup>H) and triphenyl phosphate (<sup>31</sup>P) were used as internal standards. Products precipitated from the solution were molded with KBr to form pellets and analyzed by IR spectroscopy. NMR and IR spectra were recorded on Varian (200, 300, and 600 MHz) and MIDAC FTIR instruments, respectively.

The efficiency of the catalyst operation was estimated from two parameters: the achieved concentration of formic acid and the turnover number of the catalyst (*TON*), which is equal to the ratio of the number of moles of the product formed per mole of the catalyst used.

The RhCl(PPh<sub>3</sub>)<sub>3</sub>,<sup>4</sup> HRh(PPh<sub>3</sub>)<sub>4</sub>,<sup>5</sup> Rh(acac)CO<sub>2</sub>,<sup>6</sup> HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>,<sup>7</sup> and [RhCl(CO)<sub>2</sub>]<sub>2</sub><sup>8</sup> complexes and the ligand etriolophosphite (ETPO)<sup>9</sup> were synthesized using known procedures. Commercial reagents (Fluka) RhCl<sub>3</sub>, PPh<sub>3</sub>, 2,2'-dipyridyl (2,2'-bipy), bis(1,4-diphenylphosphino)butane (dppb), bis(1,2-diphenylphosphino)ethane (dppe), OPPh<sub>3</sub>, PBu<sup>n</sup><sub>3</sub>, and DMSO were used without additional purification. Triethylamine was distilled before use.

## Results and Discussion

The results of CO<sub>2</sub> hydrogenation to formic acid using various ligands are presented in Table 1. Formic acid is

**Table 1.** Hydrogenation of CO<sub>2</sub> to HCOOH·NEt<sub>3</sub> in the presence of the Rh complexes modified by various ligands

Entry	Rh complex	Ligand	TON	[HCOOH·NEt <sub>3</sub> ] /mol L <sup>-1</sup>
1	Rh(acac)(CO) <sub>2</sub>	—	0	0
2	[RhCl(CO) <sub>2</sub> ] <sub>2</sub>	—	0	0
3	RhCl <sub>3</sub>	—	0	0
4	HRh(PPh <sub>3</sub> ) <sub>4</sub>	—	40	0.04
5	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	—	60	0.06
6	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	—	330	0.33
7	Rh(acac)(CO) <sub>2</sub>	2,2'-bipy	0	0
8	Rh(acac)(CO) <sub>2</sub>	OPPh <sub>3</sub>	0	0
9	Rh(acac)(CO) <sub>2</sub>	Dppe	30	0.03
10	Rh(acac)(CO) <sub>2</sub>	Dppb	60	0.06
11	Rh(acac)(CO) <sub>2</sub>	PPNCl	0	0
12	Rh(acac)(CO) <sub>2</sub>	ETPO	0	0
13	Rh(acac)(CO) <sub>2</sub>	PBu <sup>n</sup> <sub>3</sub>	200	0.20
14	Rh(acac)(CO) <sub>2</sub>	PPh <sub>3</sub>	500	0.50
15	[RhCl(CO) <sub>2</sub> ] <sub>2</sub>	PPh <sub>3</sub>	440	0.44
16	HRh(PPh <sub>3</sub> ) <sub>4</sub>	PPh <sub>3</sub>	470	0.47
17	RhCl <sub>3</sub>	PPh <sub>3</sub>	500	0.50
18	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	PPh <sub>3</sub>	540	0.54
19	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	PPh <sub>3</sub>	950	0.95
20	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	OPPh <sub>3</sub>	480	0.48
21	HRh(PPh <sub>3</sub> ) <sub>4</sub>	OPPh <sub>3</sub>	60	0.06

Note. Hydrogenation conditions:  $p_{\text{CO}_2} = 40$  atm,  $p_{\text{H}_2} = 20$  atm,  $[\text{Rh}] = 1 \cdot 10^{-3}$  g-at. L<sup>-1</sup>,  $[\text{NEt}_3] = 1.45$  mol L<sup>-1</sup>, P : Rh = 6, DMSO, 20 h.

not formed in the presence of the rhodium complexes without a phosphine ligand (see Table 1, entries 1–3). For example, Rh(acac)(CO)<sub>2</sub>, nonmodified or modified by 2,2'-bipy (entry 7) or OPPh<sub>3</sub> (entry 8), is inactive in CO<sub>2</sub> hydrogenation and gains activity only after the addition of phosphine (entries 9, 10, 13, and 14). [RhCl(CO)<sub>2</sub>]<sub>2</sub> and RhCl<sub>3</sub> behave similarly (entries 2, 3, 15, and 17).

All Rh complexes containing phosphine in the coordination sphere are active (see Table 1, entries 4–6). The Wilkinson complex in the presence of PPh<sub>3</sub> exhibits the highest activity (entry 19).

The catalytic properties of the Wilkinson complex are strongly affected by the conditions of formation of catalytically active sites (solvent, gaseous medium) and reaction conditions.

As can be seen in Table 2, in such solvents as heptane, benzene, and THF, the Wilkinson complex is inactive (entries 1–3), and in a DMSO solution (entries 4–8), the hydrogenation of CO<sub>2</sub> to formic acid occurs. When DMSO is replaced by water, the reaction is almost completely suppressed (entry 9). The addition of methanol (50 wt.%) to DMSO (entry 10) results in a considerable increase in the yield of formic acid and in the appearance of a significant amount of methyl formate (MF). The

**Table 2.** Hydrogenation of CO<sub>2</sub> in the presence of the Wilkinson complex<sup>a</sup>

Entry	Solvent	T/°C	Medium <sup>c</sup>	[HCOOH]	[MeOH]	[MF] <sup>b</sup>
				mol L <sup>-1</sup>		
1	Heptane	25	Ar	0	0	0
2	Benzene	25	Ar	0	0	0
3	THF	25	Ar	0	0.09	0
4	DMSO	25	Ar	0.87	0	0
5	DMSO	25	CO <sub>2</sub>	0.55	0	0
6	DMSO	25	Air	0.40	0	0
7	DMSO	25	H <sub>2</sub>	0.96	0	0
8	DMSO <sup>d</sup>	25	H <sub>2</sub>	0.26	0	0
8'	DMSO	19	H <sub>2</sub>	0.70	0	0
8''	DMSO	40	H <sub>2</sub>	0.20	0	0
9	H <sub>2</sub> O	25	H <sub>2</sub>	Traces	0.01	0
10	DMSO— —MeOH (50 wt.%)	25	H <sub>2</sub>	1.50	—	0.12
11	MeOH	25	H <sub>2</sub>	2.50	—	0.22

<sup>a</sup> Reaction conditions: RhCl(PPh<sub>3</sub>)<sub>3</sub> + 3 PPh<sub>3</sub>, 25 °C,  $[\text{Rh}] = 1 \cdot 10^{-3}$  g-at. L<sup>-1</sup>,  $p_{\text{CO}_2} = 40$  atm,  $p_{\text{H}_2} = 20$  atm, 20 h.

<sup>b</sup> MF is methyl formate.

<sup>c</sup> The medium of catalyst formation.

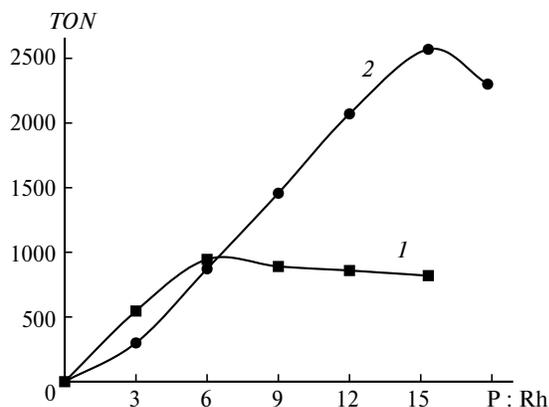
<sup>d</sup>  $[\text{Rh}] = 1 \cdot 10^{-4}$  g-at. L<sup>-1</sup>.

complete replacement of DMSO by methanol increases sharply the yields of formic acid and MF (entry 11).

The activity of the catalyst changes, depending on the gaseous atmosphere used during the dissolution of the Wilkinson complex in DMSO. The dissolution of the catalytic system in the presence of an oxidative atmosphere (in air or under the CO<sub>2</sub> pressure) decreases the yield of formic acid. The yield of the acid increases when argon or dihydrogen is used. The highest yield of formic acid is achieved when the catalyst is formed in a hydrogen atmosphere.

The yield of formic acid depends strongly on the temperature of hydrogenation (see Table 2, entries 8, 8', and 8''). It increases with the temperature increase from 19 to 25 °C but diminishes with the further temperature rise (to 40 °C).

The P : Rh ratio also has a substantial effect on the yield of formic acid. When the P : Rh ratio changes from 0 to 6 (Fig. 1, curve 1), the concentration of formic acid increases drastically. The further increase in this ratio somewhat decreases the yield of the acid. The lowest activity of the system is observed at P : Rh = 3, and the catalyst is deactivated after 4 h. Noteworthy that the plot of the change of the formic acid concentration vs. P : Rh ratio remains unchanged with a decrease in the Rh concentration by an order of magnitude. However, in this case, the maximum is more pronounced and shifts toward higher P : Rh values (see Fig. 1, curve 2).

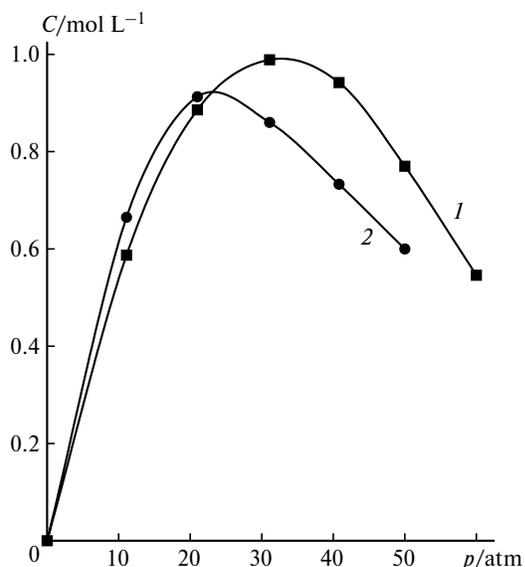


**Fig. 1.** Turnover number of the catalyst (*TON*) as a function of the P : Rh ratio ( $p_{\text{CO}_2} = 40$  atm,  $p_{\text{H}_2} = 20$  atm,  $[\text{NEt}_3] = 1.45$  mol L<sup>-1</sup>, DMSO, 20 h) at  $[\text{Rh}] = 1 \cdot 10^{-3}$  (1) and  $1 \cdot 10^{-4}$  g-at. L<sup>-1</sup> (2).

The maximum concentration and yield of formic acid were achieved at 30 atm of CO<sub>2</sub> and 20 atm of H<sub>2</sub> (*TON* = 1000) (Fig. 2). At  $p_{\text{CO}_2} = 40$  atm and  $p_{\text{H}_2} = 50$  atm, *TON* = 600.

These results suggest that for the studied interval of parameters the acid is formed with the highest yield at 25 °C,  $p_{\text{CO}_2} = 30\text{--}40$  atm,  $p_{\text{H}_2} = 20$  atm, and P : Rh = 6, and the most active catalyst is formed under a hydrogen atmosphere in polar solvents (DMSO and MeOH). Under these conditions, within 20 h *TON* ~1000 in DMSO and *TON* ~2715 (acid and MF) in MeOH were achieved.

To obtain an information on the nature of the catalytically active site of CO<sub>2</sub> hydrogenation to formic acid, we studied the interaction of the Wilkinson complexes



**Fig. 2.** Influence of the CO<sub>2</sub> pressure (1) ( $p_{\text{H}_2} = 20$  atm) and H<sub>2</sub> pressure (2) ( $p_{\text{CO}_2} = 40$  atm) on the yield of formic acid (*C*) ( $[\text{Rh}] = 1 \cdot 10^{-3}$  g-at. L<sup>-1</sup>,  $[\text{NEt}_3] = 1.45$  mol L<sup>-1</sup>, DMSO, 20 h).

**Table 3.** Products of the reaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> with the components of the reaction medium of CO<sub>2</sub> hydrogenation and characteristics of their <sup>31</sup>P NMR spectra

Reagent	Product	δ <sub>P</sub> *	J <sub>Rh-P</sub> /Hz	Refs.
Benzene	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	37.89	144	10
		54.61	191	**
DMSO	RhCl(PPh <sub>3</sub> ) <sub>2</sub> (DMSO)	20.0	125	**
	RhCl(PPh <sub>3</sub> )(DMSO) <sub>2</sub>	37.6	183	**
NEt <sub>3</sub> , DMSO	RhCl(PPh <sub>3</sub> ) <sub>2</sub> (NEt <sub>3</sub> )	46.6	154	11
NEt <sub>3</sub> , DMSO, air, H <sub>2</sub> O	OPPh <sub>3</sub>	32.5	—	**
H <sub>2</sub> , DMSO	H <sub>2</sub> RhCl(PPh <sub>3</sub> ) <sub>3</sub>	44.5, 26.1	90	12
H <sub>2</sub> , NEt <sub>3</sub> , DMSO	RhCl(PPh <sub>3</sub> ) <sub>2</sub> (NEt <sub>3</sub> )	46.6	154	11
	Rh	—	—	**
CO <sub>2</sub> , DMSO	RhCl(CO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	35.53	152	13
CO <sub>2</sub> , NEt <sub>3</sub> , DMSO	Rh(CO) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>4</sub> ***	—	—	**
	OPPh <sub>3</sub>	32.5	—	**
CO <sub>2</sub> , H <sub>2</sub> , DMSO,	H <sub>2</sub> RhCl(PPh <sub>3</sub> ) <sub>3</sub>	44.5, 26.1	90	**
	RhCl(PPh <sub>3</sub> ) <sub>2</sub> (NEt <sub>3</sub> )	46.6	154	**
NEt <sub>3</sub>	OPPh <sub>3</sub>	32.5	—	**
	Rh(CO) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>4</sub> ***	—	—	**
	Rh	—	—	**

\* Relative to the signal for P from free PPh<sub>3</sub>.

\*\* This work.

\*\*\* IR, ν/cm<sup>-1</sup>: 2038, 1919 (ν(CO)); 1085, 1182, 1431, 1475 (ν(P=O)); 694, 723, 743 (δ(Ph)). Found (%): C, 69.0; H, 5.0. Calculated (%): C, 69.8; H, 4.7.

with the components of the reaction medium (benzene, DMSO, NEt<sub>3</sub>, air, H<sub>2</sub>, and CO<sub>2</sub>) by <sup>31</sup>P NMR spectroscopy (Table 3). Solid products were analyzed by IR spectroscopy.

The data in Table 3 show that the interaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> with DMSO results in the elimination of PPh<sub>3</sub> from the coordination sphere of rhodium: DMSO rapidly displaces the first phosphine molecule, and then the second molecule is slowly displaced. This is accompanied by the appearance of signals attributed to the RhCl(PPh<sub>3</sub>)<sub>2</sub>(DMSO) and RhCl(PPh<sub>3</sub>)(DMSO)<sub>2</sub> complexes. In the absence of DMSO, when benzene is used as a solvent, no elimination of PPh<sub>3</sub> occurs.

The reaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> with Et<sub>3</sub>N in DMSO is also accompanied by the elimination of PPh<sub>3</sub> from the coordination sphere to form the RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) complex. This complex rapidly decomposes in air and in the presence of moisture traces: PPh<sub>3</sub> is rapidly oxidized to OPPh<sub>3</sub>. It was established by special experiments that PPh<sub>3</sub> is oxidized only in the presence of both oxygen and moisture present in air.

The reactions of the Wilkinson complex with H<sub>2</sub> and CO<sub>2</sub> in DMSO afford the H<sub>2</sub>RhCl(PPh<sub>3</sub>)<sub>3</sub> and RhCl(CO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> complexes, respectively. In the presence of amine, H<sub>2</sub>RhCl(PPh<sub>3</sub>)<sub>3</sub> is transformed into

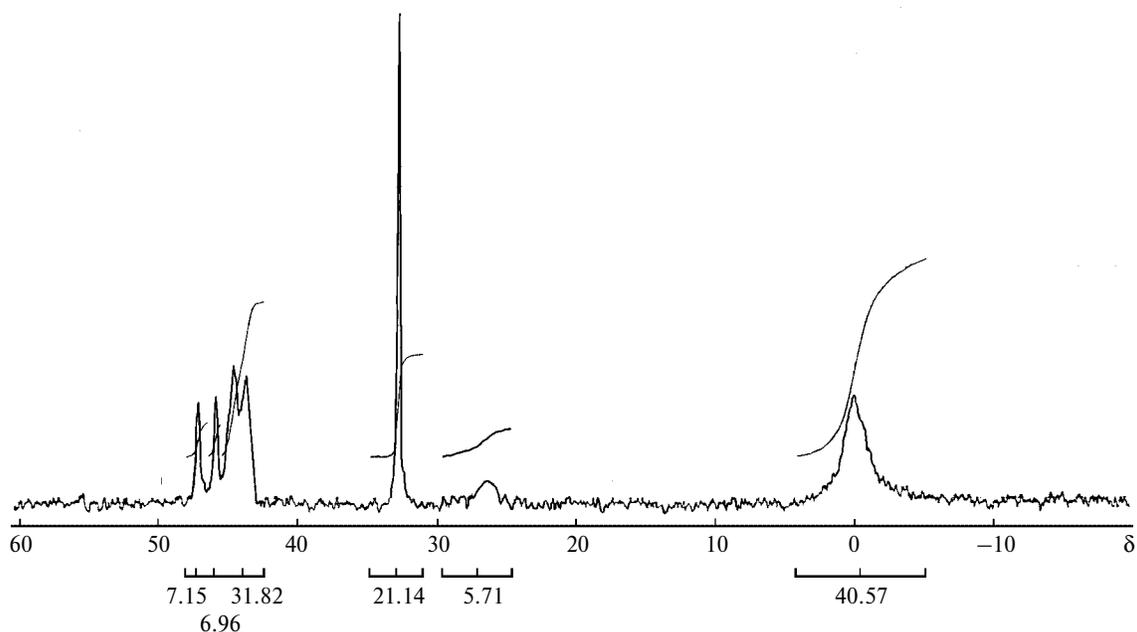


Fig. 3.  $^{31}\text{P}$  NMR spectrum of the catalytic solution of  $\text{CO}_2$  hydrogenation.

$\text{RhCl}(\text{PPh}_3)_2(\text{NEt}_3)$ , whereas it is reduced to metallic rhodium in the presence of amine in a hydrogen atmosphere. In the presence of triethylamine in a  $\text{CO}_2$  atmosphere, the  $\text{RhCl}(\text{CO}_2)(\text{PPh}_3)_2$  complex rapidly decomposes to form  $\text{OPPh}_3$  and a yellow precipitate with the  $\text{Rh}(\text{CO})_2(\text{OPPh}_3)_4$  composition. As found by special experiments,  $\text{CO}_2$  is the oxidant of  $\text{PPh}_3$  to  $\text{OPPh}_3$ . The elimination of  $\text{PPh}_3$  from  $\text{RhCl}(\text{PPh}_3)_3$  and decomposition of the  $\text{RhCl}(\text{PPh}_3)_2(\text{NEt}_3)$ ,  $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$ , and  $\text{RhCl}(\text{CO}_2)(\text{PPh}_3)_2$  complexes in the presence of  $\text{Et}_3\text{N}$  are accelerated with temperature.

When  $\text{RhCl}(\text{PPh}_3)_3$  reacts simultaneously with  $\text{DMSO}$ ,  $\text{NEt}_3$ ,  $\text{H}_2$ , and  $\text{CO}_2$ ,  $\text{CO}_2$  is hydrogenated to formic acid. The  $\text{RhCl}(\text{PPh}_3)_2(\text{NEt}_3)$  and  $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$  complexes,  $\text{PPh}_3$ , and  $\text{OPPh}_3$  were found in the hydrogenation product. The most characteristic  $^{31}\text{P}$  NMR spectrum of the catalytic solution is presented in Fig. 3. It contains signals corresponding to the  $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$  ( $\delta_{\text{P}} 44.5$ ,  $J_{\text{Rh-P}} = 90$  Hz and  $\delta_{\text{P}} 26.1$ ) and  $\text{RhCl}(\text{PPh}_3)_2(\text{NEt}_3)$  ( $\delta_{\text{P}} 46.6$ ,  $J_{\text{Rh-P}} = 154$  Hz) complexes and signals assigned to triphenylphosphine ( $\delta_{\text{P}} 0$ ) and  $\text{OPPh}_3$  ( $\delta_{\text{P}} 32.5$ ). An internal standard was added to a catalytic solution for the quantitative determination of concentrations of these phosphorus-containing compounds. Figure 4 shows the changes in the concentrations of formic acid,  $\text{PPh}_3$ ,  $\text{OPPh}_3$ , and rhodium complexes detected during  $\text{CO}_2$  hydrogenation in samples taken in the time moments corresponding to points A, B, C, and D.

In point A the acid has not yet formed. The  $^{31}\text{P}$  NMR spectrum of the sample contains signals attributed to  $\text{PPh}_3$ ,  $\text{OPPh}_3$ , and  $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$  (a portion of this complex exists in the insoluble form as a yellow powder).

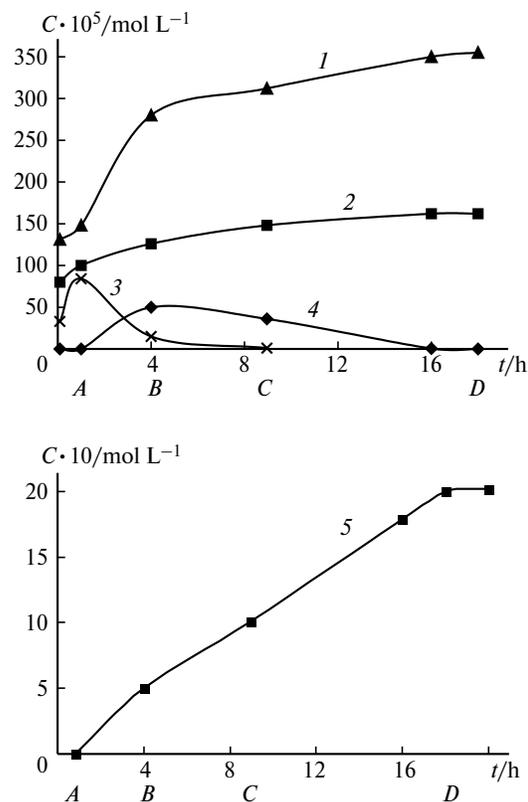


Fig. 4. Concentration plots obtained from the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra of the catalytic solution during  $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed  $\text{CO}_2$  hydrogenation to formic acid ( $[\text{Rh}] = 1 \cdot 10^{-2}$  g-at.  $\text{L}^{-1}$ ,  $\text{P} : \text{Rh} = 6$ ,  $[\text{NEt}_3] = 1.45$  mol  $\text{L}^{-1}$ ,  $\text{DMSO}$ ):  $\text{PPh}_3$  (1);  $\text{OPPh}_3$  (2);  $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$  (3);  $\text{RhCl}(\text{PPh}_3)_2(\text{NEt}_3)$  (4), and  $\text{HCOOH}$  (5).

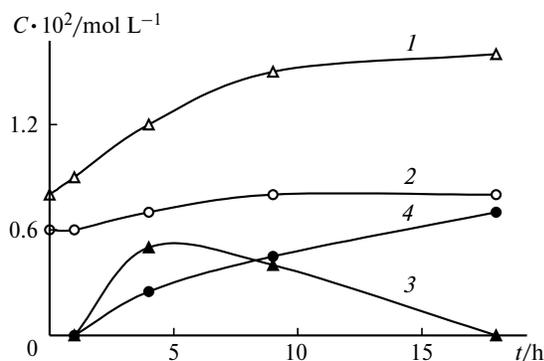


Fig. 5. Changes in the concentrations of OPPh<sub>3</sub> (1, 2) and RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) (3, 4) in time at different P:Rh ratios equal to 6 (1, 3) and 9 (2, 4); RhCl(PPh<sub>3</sub>)<sub>3</sub>, [Rh] = 1 · 10<sup>-2</sup> g-at. L<sup>-1</sup>, [NEt<sub>3</sub>] = 1.45 mol L<sup>-1</sup>, DMSO.

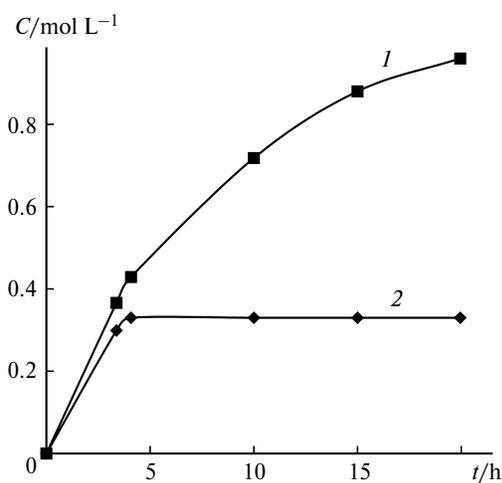


Fig. 6. Hydrogenation of CO<sub>2</sub> in the presence of the Wilkinson complex: RhCl(PPh<sub>3</sub>)<sub>3</sub> + 6 PPh<sub>3</sub> (1), RhCl(PPh<sub>3</sub>)<sub>3</sub> (2); [Rh] = 1 · 10<sup>-3</sup> g-at. L<sup>-1</sup>, p<sub>CO<sub>2</sub></sub> = 40 atm, p<sub>H<sub>2</sub></sub> = 20 atm, [NEt<sub>3</sub>] = 1.45 mol L<sup>-1</sup>, DMSO, 20 h.

The formation of formic acid starts in point B. The spectra exhibited additional signals assigned to RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>). The concentration of H<sub>2</sub>RhCl(PPh<sub>3</sub>)<sub>3</sub> decreased, and that of PPh<sub>3</sub> increased.

In point C the hydrogenation of CO<sub>2</sub> occurs intensely; the spectra contain signals characteristic of RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>), PPh<sub>3</sub>, and OPPh<sub>3</sub>.

The hydrogenation process has stopped in point D, despite an excess of amine in the reaction medium. The spectrum does not exhibit signals from the phosphine-rhodium complexes. The concentrations of PPh<sub>3</sub> and OPPh<sub>3</sub> increased significantly.

The presented results allow a relation between the formation of formic acid and the presence of the RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) complex to be established, namely, the beginning and end of CO<sub>2</sub> hydrogenation coincide with the appearance and disappearance of this complex, respectively. Based on the data obtained, we can suggest that the RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) complex is a precursor of the catalytically active complex.

The RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) complex decomposes during hydrogenation to yield free PPh<sub>3</sub>, the product of its oxidation OPPh<sub>3</sub>, metallic rhodium, and Rh(CO)<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>. Taking into account the data in Table 3, we can say that the formation of metallic rhodium is favored by the presence of hydrogen and triethylamine.

The decomposition of RhCl(PPh<sub>3</sub>)<sub>2</sub>(NEt<sub>3</sub>) and oxidation of PPh<sub>3</sub> to OPPh<sub>3</sub> (Fig. 5) are inhibited in the presence of an excess of phosphine. Metallic rhodium is not formed, and the yield of formic acid increases significantly (Fig. 6).

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