## Transformations of formaldehyde and glycolaldehyde during the hydroformylation of formaldehyde in the presence of rhodium catalysts

N. N. Ezhova,\* G. A. Korneeva, E. V. Slivinsky, and R. A. Aronovich

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 117912 Moscow, Russian Federation, Fax: +7 (095) 230 2224

Hydroformylation of formaldehyde to give glycolaldehyde (GA) in the presence of RhCl(PPh<sub>3</sub>)<sub>3</sub>, RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, or the RhCl<sub>3</sub> + PPh<sub>3</sub> system in *N*,*N*-dimethylacetamide was studied. The hydroformylation is accompanied by the Cannizzaro—Tishchenko reaction, condensation of CH<sub>2</sub>O with GA to give C<sub>3</sub>—C<sub>16</sub> polyoxyaldehydes (POA), and dimerization of GA. The formation of POA, which probably occurs through coordination of GA with a Rh atom, predominates among the side reactions. The optimum conditions for hydroformylation of CH<sub>2</sub>O were found to be: RhCl<sub>3</sub> + PPh<sub>3</sub> as the catalyst,  $T \le 383$  K,  $p_{CO+H_2} \ge 12$  MPa,  $[H_2O] \le 1.8$  mol L<sup>-1</sup>,  $[Rh] \le 2.5 \cdot 10^{-3}$  g-at. L<sup>-1</sup>, and  $[CH_2O] \le 0.03$  g L<sup>-1</sup>. At a substrate conversion of 62—67 %, the selectivity of GA formation reaches 96 %, and the yield is 60—65 %.

Key words: formaldehyde, hydroformylation; glycolaldehyde; rhodium catalysts.

Hydroformylation of formaldehyde according to the reaction:

$$CH_2O + CO + H_2 \longrightarrow HOCH_2CHO$$
 (1)

allows one to prepare glycolaldehyde (GA), which is an intermediate product in the synthesis of valuable chemicals such as ethylene glycol, glycoxal, glycolic and oxalic acids, and biologically active compounds.

The results of investigations of the hydroformylation of formaldehyde<sup>1-3</sup> make it possible to suggest that the substrate and the reaction product are involved in various side and secondary transformations, which diminish the selectivity of the formation of GA. In the present work we studied transformations of CH<sub>2</sub>O and HOCH<sub>2</sub>CHO in the course of hydroformylation in the presence of rhodium catalysts in an N,N-dimethylacetamide (DMAA) solution and determined the most favorable conditions for the target reaction.

## Experimental

Hydroformylation of CH<sub>2</sub>O was carried out in a stainlesssteel 250-mL autoclave equipped with a stirrer. The catalyst, DMAA, and paraformaldehyde (PF) or Formalin were placed in the autoclave, and the mixture was heated to the required temperature. Then the synthesis gas (CO + H<sub>2</sub>) was pumped in, and the pressure was increased to the operating pressure. Samples of the liquid product were withdrawn in the course of hydroformylation, the pressure was maintained constant, and the gas consumed in the reaction was replenished from a calibrated 9-mL vessel.

The liquid products were identified by GC-FTIR spectroscopy on an LFS-113V spectrometer. A packed column (l = 3 m, d = 2 mm) filled with Polychrom-1 with 10 % poly(ethylene glycol adipinate) was used for the analysis. Polyoxyaldehydes were analyzed as silyl derivatives (using trimethylchlorosilane and hexamethyldisilazane as silylating reagents) on a column with Chromaton N-AW with 5 % SE-30.

The conversion of  $CH_2O$  and the yield of GA and the selectivity of its formation were calculated based on the number of moles of the starting  $CH_2O$ . The selectivity of the formation of GA (%) was defined as the ratio of the yield of GA to the conversion of  $CH_2O$ . IR spectra were recorded on a Specord M-80 spectrometer; electronic absorption spectra were obtained on a Specord UV-Vis spectrometer.

The Rh complexes were prepared by the standard procedures.  $^{4\!-\!8}$ 

## **Results and Discussion**

The results of the hydroformylation of  $CH_2O$  in polar solvents in the presence of Rh complexes of various compositions are presented in Table 1. The highest yield of GA was achieved when hydroformylation was carried out with Wilkinson's complex (see Table 1, run 6) or with rhodium carbonyl chloride modified with triphenylphosphine (run 18) in DMAA. For these conditions, side and secondary reactions were studied. In addition to GA and unchanged  $CH_2O$ , the reaction mixture contained methanol, formic acid, and POA of

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 1, pp. 75–78, January, 1995. 1066-5285/95/4401-0069 \$12.50 © 1995 Plenum Publishing Corporation

**Table 1.** Hydroformylation of formaldehyde in the presence of rhodium complexes (383 K,  $p_{CO+H_2} = 13$  MPa, [PF] = 0.03 g mL<sup>-1</sup>, 60 mL of a solvent, [Rh] =  $2.5 \cdot 10^{-3}$  g-at. L<sup>-1</sup>, 2.5 h)

Run	Rhodium complex <sup>a</sup>	Solvent	Yield of GA (mol. %)	Selectivity of the formation of GA (%)
1	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Water	0	0
2	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	$CH_2Cl_2$	0	0
3	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	n-Butanol	0	0
4	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetone	10	50
5	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	DMF	43	59
6	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	DMAA	50	55
7	$RhCl(CO)L_2$	Water	0	0
8	$RhCl(CO)L_2$	n-Butanol	0	0
9	$RhCl(CO)L_2$	DMAA	31	45
10 <sup>b</sup>	$RhCl(CO)L_2$	DMAA	16	17
11	$Rh_4(CO)_{12}$	n-Butanol	0	0
12	$Rh_4(CO)_{12}$	DMAA	17	39
13	$Rh(acac)(CO)_2$	<i>p</i> -Xylene	2	80
14	RhH(CO)(PPh <sub>3</sub> ) <sub>3</sub>	DMAA	39	54
15	$[RhCl(CO)_2]_2$	p-Xylene	0	0
16	$[RhCl(CO)_2]_2$	DMAA	7	52
17	RhCl(CO)(PBu) <sub>2</sub>	DMAA	7	46
18	RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	DMAA	50	55

<sup>*a*</sup> L = PPh<sub>2</sub>[m-(SO<sub>3</sub>Na)C<sub>6</sub>H<sub>4</sub>]. <sup>*b*</sup>For Formalin (5 mL, 36 % formaldehyde).

various molecular weights  $(C_3-C_{16})$ . One may assume that, along with hydroformylation (reaction (1)), the Cannizzaro—Tishchenko reaction (reaction (2)), hydrogenation of CH<sub>2</sub>O to give methanol (reaction (3)), and condensation of CH<sub>2</sub>O with GA to give POA (reaction (4)) occur.

2 CH <sub>2</sub> O + H <sub>2</sub> O	CH <sub>3</sub> OH + HCOOH	(2)
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 $CH_2O + H_2 \longrightarrow CH_3OH$  (3)

$$x \operatorname{CH}_2\operatorname{O} + y \operatorname{HOCH}_2\operatorname{CHO} \longrightarrow \operatorname{POA}$$
 (4)

The calculation of the material balance for the hydroformylation confirms the formation of methanol according to reactions (2) and (3) and the formation of POA by reaction (4), and also indicates that GA is formed only by hydroformylation of  $CH_2O$  (see reaction (1)) without participation of the known<sup>9</sup> condensation of  $CH_2O$ , which also yields GA (reaction (5)).

 $2 \text{ CH}_2 \text{O} \longrightarrow \text{HOCH}_2 \text{CHO}$  (5)

It has been shown previously<sup>10</sup> that GA readily undergoes dimerization (reaction (6)).

$$2 \text{ HOCH}_2\text{CHO} \longrightarrow \bigcup_{HO} \bigcup_{O} \bigcup_{O}$$

The results of an evaluation of the thermodynamic probability of the hydroformylation of  $CH_2O$  according to pathways (1) and (7) presented in Table 2 indicate that a high conversion of  $CH_2O$  in hydroformylation at elevated temperatures may be expected only when the dimeric form of GA is produced.

An IR spectroscopic analysis of a solution of the original solid glycolaldehyde dimer in DMAA showed that the system contained no HOCH<sub>2</sub>CHO: the spectrum exhibited no absorption band (AB) at 1772 cm<sup>-1</sup>, which is normally recorded in the IR spectra of the GA monomer in the gas phase or in solutions in heptane or CH<sub>2</sub>Cl<sub>2</sub>. Thus, in DMAA, the equilibrium of reaction (6) is shifted to the right, so the GA formed in hydroformylation may dimerize. (Under the conditions of GLC analysis of liquid products, the dimer of GA is converted into HOCH<sub>2</sub>CHO, as has been found by GC-FTIR spectroscopy.)

Thus, the following side transformations of  $CH_2O$  occur at noticeable rates during hydroformylation: the Cannizzaro—Tishchenko reaction, hydrogenation of  $CH_2O$  to give methanol, and condensation of  $CH_2O$  with GA; dimerization of GA also apparently occurs.

Figure 1 shows the plots of the conversion of  $CH_2O$  in reactions (1)-(4) vs. the duration of hydroformyla-

Table 2. The results of the evaluation of the thermodynamic probability of hydroformylation of formaldehyde

Pathway	T/K	$\Delta G$ /kJ mol <sup>-1</sup>	K *	Conversion of $CH_2O$ at various $CH_2O$ : $CO$ : $H_2$ ratios**			
				1:1:1	1 : 50 : 50	1 : 75 : 75	
$CH_2O + CO + H_2 \rightarrow HOCH_2CHO$ (1)	300 400 500	-14.54 10.96 36.16	$3.39 \cdot 10^{2} 3.72 \cdot 10^{-2} 2.00 \cdot 10^{-2}$	83.6900 0.4100 0.0020	98.8100 0.9020 0.0040	98.8200 0.9080 0.0040	
2 (CH <sub>2</sub> O + CO + H <sub>2</sub> ) $\rightarrow$ 2 HOCH <sub>2</sub> CHO (7)	300 400 500	-165.99 -80.33 0.04	$7.61 \cdot 10^{28} 3.04 \cdot 10^{10} 9.90 \cdot 10^{-1}$	100.0000 100.0000 99.2000	100.0000 100.0000 100.0000	100.0000 100.0000 100.0000	

*Note.* The calculations were carried out for ideal gases according to standard procedures.<sup>11,12</sup> The total pressure was taken to be 0.1 MPa. \* The equilibrium constant. \*\* The molar ratio.



Fig. 1. The dependence of the conversion of  $CH_2O$  for reactions (1)-(4) (curves 1-4, respectively) on the duration of hydroformylation (for conditions, see Table 1, run 6). For I-IV, see in the text.

tion.\* One can see that the Cannizzaro—Tishchenko reaction (see reaction (2)) proceeds at a noticeable rate during the period preceding hydroformylation when depolymerization of PF to give CH<sub>2</sub>O occurs (section I), while condensation of CH<sub>2</sub>O with GA to give POA is pronounced at the final stage of hydroformylation (section IV), after the accumulation of GA in the reaction mixture. The Cannizzaro—Tishchenko reaction is not catalyzed by the Rh complex, and its rate does not depend on its presence in the reaction mixture (Table 3, runs *1* and *2*). The other transformations are catalytic: they accelerate as the concentration of RhCl(PPh<sub>3</sub>)<sub>3</sub> in the reaction mixture increases (see Table 3). The fact that reaction (3) accompanies formation of GA according to pathway (1) during the initial 2–5 min of hydroformylation (see Fig. 1, section II) may be associated with the fact that during hydroformylation RhCl(PPh<sub>3</sub>)<sub>3</sub> is converted into structures possessing various catalytic activities in hydrogenation (see reaction (3)) and in the target reaction (1).

As follows from the data of Table 3, condensation of CH<sub>2</sub>O with GA to give POA is the main side reaction that lowers the selectivity of the formation of GA during hydroformylation. It cannot be ruled out that this reaction occurs through the coordination of the GA monomer (involving the carbonyl group) to the Rh atom. This assumption was based on the results of a study of the interaction of GA with RhCl(PPh<sub>3</sub>)<sub>3</sub> at 293 K by electronic and IR spectroscopy. In fact, in the electronic absorption spectrum of a DMAA solution of  $RhCl(PPh_3)_3$ , a decrease in the intensity of the band in the 360 nm region typical of a solution of RhCl(PPh<sub>3</sub>)<sub>3</sub> in an amide<sup>13</sup> and a shift of the charge-transfer band to higher frequencies were observed after the introduction of GA (the GA : Rh complex molar ratio was 98 : 1). These changes in the spectrum indicate that in the presence of GA, a new Rh complex was formed. In the region of carbonyl group vibrations of the IR spectrum of GA in an *n*-heptane or CH<sub>2</sub>Cl<sub>2</sub> solution containing RhCl(PPh<sub>3</sub>)<sub>3</sub>, in addition to the absorption band at 1772 cm<sup>-1</sup> typical of the CO stretching vibrations in free HOCH<sub>2</sub>CHO, a band at 1736 cm<sup>-1</sup> probably associated with the coordination interaction of the carbonyl group of the GA monomer with the Rh atom was recorded.

Dimerization (see reaction (6)) obviously competes with condensation (4) involving the monomer of GA. Therefore, the selectivity of the formation of GA in the hydroformylation of  $CH_2O$  is predominantly determined by the ratio between the rates of reactions (4) and (6).

In the course of hydroformylation of  $CH_2O$ , the rate of reaction (6) is greater in magnitude than that of reaction (4) only in the initial periods (II and III, see Fig. 1)., *i.e.*, at relatively low conversions of  $CH_2O$  (50–55 %).

Since dimerization (cyclization) of aldehydes is catalyzed by weak acids,<sup>14</sup> we managed to increase the

Table 3. The effect of the concentration of  $RhCl(PPh_3)_3$  on transformations of  $CH_2O$  in the course of hydroformylation

Run	$[RhCl(PPh_3)_3] \cdot 10^3$ /mol L <sup>-1</sup>	Conv in re	version actions	The selectivity of the formation		
		(1)	(2)	(3)	(4)	of GA (%)
1	0	0	1	0	0	0
2	1.27	45	1	1	12	76
3	2.50	60	1	2	15	77
4	5.00	55	1	3	27	64
5	10.00	40	1	5	50	42

*Note.* The duration of the reaction was 90 min. For the other conditions, see Table 1.

<sup>\*</sup> Conversion of CH<sub>2</sub>O in reaction (4) was calculated from the equation:  $K_{POA} = K_{CH_2O} - \Sigma K_i$ , where  $K_{POA}$  is the conversion of CH<sub>2</sub>O into polyoxyaldehydes,  $K_{CH_2O}$  is the overall conversion of CH<sub>2</sub>O, and  $K_i$  (i = 1, 2, 3) is the conversion of CH<sub>2</sub>O according to reactions (1), (2), and (3), respectively;  $K_1$  is equal to the yield of GA,  $K_2$  is equal to the sum of the yields of formic acid and methanol in reaction (2), and  $K_3$  is equal to the yield of methanol in reaction (3).

Run	<i>р</i> <sub>СО+Н2</sub> /MPa	<i>T/</i> K	[PF] /g mL <sup>-1</sup>	[Rh] /g-at. L <sup>–1</sup>	[H <sub>2</sub> O] /mol L <sup>-1</sup>	/mol $L^{v_0^a}$ min <sup>-1</sup>	Conversion of $CH_2O$ (%) in reactions		The selectivity of the formation of $GA^b$ (%)		
							(1)	(2)	(3)	(4)	
1	1	383	0.03	25.00	0.5	0.000	0	1.0	0.0	0	0
2	3	383	0.03	25.00	0.5	0.001	5	1.0	6.0	0	42
3	8	383	0.03	25.00	0.5	0.003	24	1.0	5.0	0	80
4	10	383	0.03	25.00	0.5	0.004	30	1.0	0.5	0	95
5	12	383	0.03	25.00	0.5	0.005	40	1.0	0.5	0	96
6	13	383	0.03	25.00	0.5	0.008	52	1.0	0.5	0	97
7	14	383	0.03	25.00	0.5	0.008	52	1.0	0.5	0	97
8	13	373	0.03	25.00	0.5	0.005	45	1.0	0.5	0	97
9	13	393	0.03	25.00	0.5	0.010	42	1.0	0.5	15	72
10	13	403	0.03	25.00	0.5	0.012	35	1.0	0.5	23	59
11	13	383	0.06	25.00	0.5	0.016	49	1.0	0.5	12	78
12	13	383	0.09	25.00	0.5	0.024	37	1.0	0.5	28	56
13	13	383	0.30	25.00	0.5	0.036	10	1.0	0.5	67	13
14	13	383	0.03	1.27	0.5	0.004	27	1.0	0.5	0	95
15	13	383	0.03	5.00	0.5	0.016	49	1.0	2.0	6	84
16	13	383	0.03	10.00	0.5	0.050	50	1.0	5.0	20	66
17	13	383	0.03	2.50	0.1	0.001	17	0.3	0.5	0	96
18	13	383	0.03	2.50	1.8	0.024	60	1.5	0.5	0	96
19	13	383	0.03	2.50	3.0	0.030	55	2.0	0.5	12	79

Table 4. Transformations of  $CH_2O$  during hydroformylation in the presence of the  $RhCl_3 + PPh_3$  system in a DMAA solution

<sup>a</sup> The initial rate of the formation of GA. <sup>b</sup> Duration of the reaction was 60 min.

rate of reaction (6) and to carry out selective hydroformylation at high conversions of  $CH_2O$  by using a weakly acidic medium (pH 5.5). RhCl<sub>3</sub> (possessing acidic properties) in combination with PPh<sub>3</sub> was used as the catalyst. The selectivity of the formation of GA amounted to 87–96 % at a conversion of  $CH_2O$  of 62–67 %, and the yield of GA was 60–65 %.

Table 4 presents the results of the study of the effect of the parameters of the process and composition of the reaction medium on the transformations of CH<sub>2</sub>O in the course of its hydroformylation in the presence of the  $RhCl_3 + PPh_3$  system (at a  $PPh_3$  :  $RhCl_3$  molar ratio of 2:1). The target reaction occurs at noticeable rates at  $p \ge 3$  MPa. It accelerates as the pressure increases from 3 to 13 MPa and also as the temperature or the concentration of PF, the rhodium catalyst, or water increase. When p < 12 MPa, hydrogenation of CH<sub>2</sub>O to give methanol (see reaction (3)) is intensified, and when the temperature increases (> 383 K) or the concentration of PF, the rhodium catalyst, or water increases, then condensation of CH<sub>2</sub>O with GA to give POA accelerates, and this decreases the selectivity of the formation of GA. An increase in the proportion of water in the reaction solution also results in intensification of the Cannizzaro-Tishchenko reaction, but the conversion of CH<sub>2</sub>O according to this reaction does not exceed 1.5 % at  $[\tilde{H}_2O] \le 1.8 \text{ mol } L^{-1}$ , and it has no substantial effect on the selectivity of the formation of the target product.

The results of the study indicate that the following conditions are appropriate for the selective hydroformylation of  $CH_2O$  in a DMAA solution in the presence of the RhCl<sub>3</sub> + PPh<sub>3</sub> system to produce GA:  $T \le 383$  K, 12 MPa  $\le p_{CO+H_2} < 14$  MPa, [PF]  $\le 0.03$  g mL<sup>-1</sup>, [Rh]  $\le 2.5 \cdot 10^{-3}$  g-at. L<sup>-1</sup>, [H<sub>2</sub>O]  $\le 1.8$  mol L<sup>-1</sup>, and incomplete conversions of the substrate. Hydroformylation with high selectivity with respect to the target product (87–96 %) at a relatively high conversion of CH<sub>2</sub>O (62–67 %) and a relatively high yield of GA (60–65 %) occurs at T = 383 K,  $p_{CO+H_2} = 13$  MPa, [PF] = 0.03 g mL<sup>-1</sup>, [Rh] =  $2.5 \cdot 10^{-3}$  g-at. L<sup>-1</sup>, [H<sub>2</sub>O] = 1.8 mol L<sup>-1</sup>.

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Received July 7, 1994