# Study of hydroformylation of formaldehyde in the presence of rhodium catalysts by *in situ* IR spectroscopy and the kinetic technique

*N. N. Ezhova,* G. A. Korneeva, V. I. Kurkin, and E. V. Slivinsky*

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

Carbonylrhodium complexes formed during hydroformylation of $CH_2O$ from various rhodium precursors were investigated by *in situ* IR spectroscopy. It was found that under the conditions of the hydroformylation of $CH_2O$ in *N,N*-dimethylacetamide (DMAA), $RhH(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $RhCl(PPh_3)_3$, $RhCl(CO)(PBu_3)_2$, and $[RhCl(CO)_2]_2$ form complex systems that necessarily contain anionic complexes, $[Rh(CO)_2L_x(DMAA)_y]^-$ ($L = PPh_3$, $PBu_3$, $x = 1$ to 2, $y = 1$ to 0; $[Rh(CO)_4]^-$). The participation of ionic structures in the hydroformylation of $CH_2O$, most likely, in the step of the activation of $CH_2O$, was proven by kinetic techniques.

**Key words:** formaldehyde, hydroformylation, rhodium complexes, *in situ* IR spectroscopy.

Hydroformylation of formaldehyde

$$CH_2O + CO + H_2 \rightarrow HOCH_2CHO, \qquad (1)$$

catalyzed by rhodium, cobalt, or ruthenium complexes, yielding glycolaldehyde, is the only known example of the hydroformylation of a carbonyl group.

Two types of suggestions concerning the mechanism of this reaction exist. Some authors believe that the hydroformylation of $CH_2O$ occurs similarly to the known reaction of olefins in which metal hydrocarbonyls act as catalytic sites.[1—3] Other authors suggest that the catalytic cycle of the hydroformylation of $CH_2O$ involves anionic metal complexes.[4—6] In general, the mechanism of reaction (1) and, specifically, the nature of the catalytic sites remain unknown.

In this work we present the results of *in situ* IR and kinetic studies of the nature of the active sites of the hydroformylation of $CH_2O$ formed from rhodium complexes of various compositions under the reaction conditions in an *N,N*-dimethylacetamide (DMAA) solution.

## Experimental

Hydroformylation of formaldehyde was carried out in an autoclave IR cell with electric heating and an electromagnetic stirrer.[7] The autoclave IR cell was placed in a Specord M-80 spectrophotometer and heated to 373 K, a DMAA solution of a rhodium complex and formaldehyde ($V$ = 10 mL, [Rh] = $1 \cdot 10^{-2}$ g-at $L^{-1}$, [$CH_2O$] = 1 mol $L^{-1}$) was introduced into the cell, and then synthesis gas of the composition 1CO : $1H_2$ (mol.) or 1CO : $1D_2$ was pumped in until the working pressure (6 MPa) was achieved. In the course of hydroformylation the IR spectra of the reaction solution were recorded, and samples of the liquid product were taken and analyzed by GLC using a steel column (2 m×3 mm) packed with Polychrom-1 with poly(ethylene glycol adipinate) (10 % (w/w)).

The kinetic experiments were carried out according to the known procedure[8] at a rate of stirring of 1200 revolutions per minute, which ensured that the hydroformylation of $CH_2O$ occurred in the kinetic region (variation of the number of revolutions of the stirrer from 300 to 1400 per minute did not result in change in the rate of the reaction). The rate of the hydroformylation of $CH_2O$ was evaluated from the rate of the formation of glycolaldehyde.

The rhodium complexes were synthesized using the standard procedures.[9—13]

## Results and Discussion

The results of hydroformylation of formaldehyde in the presence of rhodium complexes of various compositions are presented in Table 1. These data imply that $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$, $RhCl(CO)(PBu_3)_2$, and $[RhCl(CO)_2]_2$ complexes in DMAA are active in reaction (1).

To elucidate the nature of the active sites of the catalysts of hydroformylation of $CH_2O$, we studied the composition of carbonylrhodium complexes formed from the above-listed precursors under the reaction conditions by *in situ* IR spectroscopy. The regions of the carbonyl and Rh—H vibrations of the IR spectra of the reaction solutions are shown in Fig. 1. The spectra for $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ are not shown in Fig. 1, since they are similar to the spectrum recorded in the presence of $RhH(CO)(PPh_3)_3$. The assignment of

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1066—1069, June, 1995.

**Table 1.** Hydroformylation of formaldehyde in the presence of rhodium complexes

| Complex | Solvent | $w_0$ /mol L min$^{-1}$ | $K_{CH_2O}$ (%) |
|---|---|---|---|
| $RhCl(PPh_3)_3$ | DMMA | 0.017 | 55 |
| $RhCl(PPh_3)_3$ + $47PPh_3$ | DMMA | 0 | 0 |
| $RhCl(CO)(PPh_3)_2$ | DMMA | 0.017 | 55 |
| $RhH(CO)(PPh_3)_3$ | DMMA | 0.009 | 40 |
| $RhH(CO)(PPh_3)_3$ + $47PPh_3$ | DMMA | 0 | 0 |
| $RhCl(CO)(PBu_3)_2$ | DMMA | 0.002 | 7 |
| $[RhCl(CO)_2]_2$ | DMMA | 0.002 | 7 |
| $Rh(acac)(CO)_2$ | DMMA | 0 | 0 |
| $[RhCl(CO)_2]_2$ | *n*-Ксилол | 0 | 0 |
| $RhCl(PPh_3)_3$ | *n*-Ксилол | 0 | 0 |
| $RhH(CO)(PPh_3)_3$ | Гептан | 0 | 0 |

*Note.* $T$ = 383 K, $p_{1CO+1H_2}$ = 13 MPa, [Rh] = $2.5 \cdot 10^{-3}$ g-at L$^{-1}$, 60 mL of solvent, 1.8 g of paraformaldehyde, $\tau$ = 60 min.

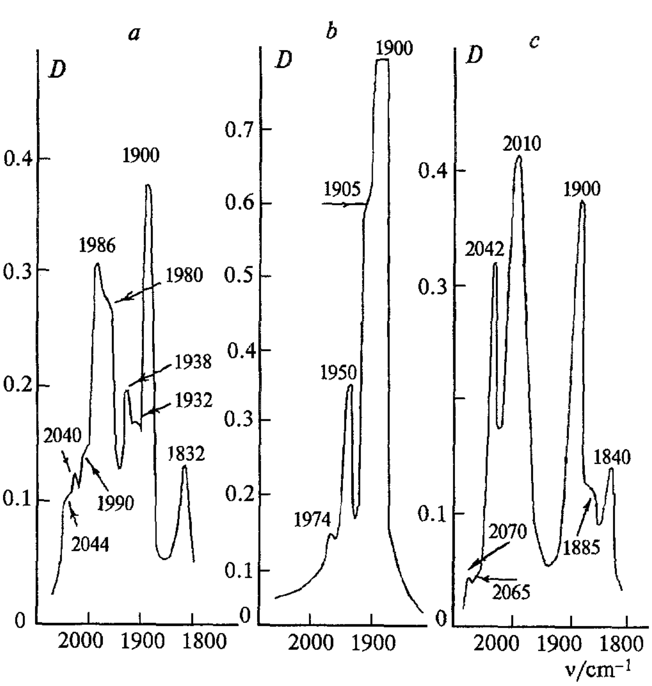

**Fig. 1.** The *in situ* IR spectra of the reaction mixture obtained by the hydroformylation of $CH_2O$ in DMAA in the presence of $RhH(CO)(PPh_3)_3$ (*a*), $RhCl(CO)(PBu_3)_2$ (*b*), or $[RhCl(CO)_2]_2$ (*c*) ($T$ = 373 K, $p_{1CO:1H}$ = 6 MPa, [Rh] = $1 \cdot 10^{-2}$ g-at L$^{-1}$, 10 mL of DMAA, $[CH_2O]$ = 1 mol L$^{-1}$, $\tau$ = 1 min).

the absorption bands (AB) given in Table 2 was based on the literature data[4,14–18] and on the results of experiments in which $H_2$ in the synthesis gas was replaced by $D_2$, which made it possible to distinguish between the vibrations of the Rh—H bond and the CO groups. From the data presented in Table 2 it follows that, under the reaction conditions, all of the complexes active in reaction (1) produce systems that involve, along with the neutral complexes, anionic complexes ($[Rh(CO)_4]^-$ and $[Rh(CO)_2L_x(DMAA)_y]^-$, where $x$ = 1 to 2, $y$ = 1 to 0, L = $PPh_3$, $PBu_3$.).

The rate of hydroformylation of $CH_2O$ depends on the concentration of anionic carbonylrhodium complexes and does not depend on the concentration of neutral complexes. In fact, in the case of $PPh_3$-containing complexes, the initial rate of reaction (1) is proportional to the initial concentration of $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$, which is characterized by the optical densities of AB at 1990 and 1932 cm$^{-1}$ (Fig. 2). According to the IR spectroscopy data, the formation of the anionic complex from $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ is hampered by an excess of $PPh_3$, when DMAA is used as the solvent, or by the use of hydrocarbon solvents. Under the conditions where anionic complexes, unlike neutral complexes, are not produced (in hydrocarbon solvents or with an excess of $PPh_3$ in DMAA at P/Rh ≥50 g-at/g-at), hydroformylation does not occur (see Table 1).

The direct dependence of the rate of reaction (1) on the concentration of the anionic carbonylrhodium complexes in the reaction solution suggests that these complexes act as the sites of the hydroformylation of $CH_2O$. Protons can act as counter ions for the anionic complexes.[4,5] The increase in the rate of reaction (1) with increase in the concentration of protons in the reaction mixture, *i.e.*, with a decrease in the pH (Fig. 3, *a*),

**Table 2.** Assignment of the absorption bands in the IR spectra of the reaction solutions of the hydroformylation of formaldehyde in DMAA in the presence of rhodium complexes

| Starting complex | ν/cm$^{-1}$ (assignment) | Complex in the reaction solution | Reference |
|---|---|---|---|
| $RhH(CO)(PPh_3)_3$ | 1900 (CO) | $[Rh(CO)_4]^-$ | 4 |
| | 2044 (CO), 1986 (CO), 1832 ($\mu_{CO}$) | $[Rh(CO)_2(PPh_3)_x(DMMA)_y]_2$, $x$ = 1÷2, $y$ = 1÷0 | 14 |
| | 2040 (Rh—H), 1980 (CO), 1938 (CO) | $RhH(CO)_2(PPh_3)_2$ | 4,15 |
| | 1990 (CO), 1932 (CO) | $[Rh(CO)_2(PPh_3)_x(DMMA)_y]^-$, $x$ = 1÷2, $y$ = 1÷0 | 16 |
| $RhCl(CO)(PBu_3)_2$ | 1950 (CO) | $RhCl(CO)(PBu_3)_2$ | 17 |
| | 1900 (CO) | $[Rh(CO)_4]^-$ | 4 |
| | 1905 (CO), 1974 (CO) | $[Rh(CO)_2(PBu_3)_x(DMMA)_y]^-$, $x$ = 1÷2, $y$ = 1÷0 | 16,17 |
| $[RhCl(CO)_2]_2$ | 2042 (CO), 2010 (CO), 1840 (μCO) | $[Rh_5(CO)_{15}]^-$ | 18 |
| | 1900 (CO) | $[Rh(CO)_4]^-$ | 4 |
| | 2070 (CO), 2065 (CO), 1885 (CO) | $Rh_4(CO)_{12}$ | 15 |

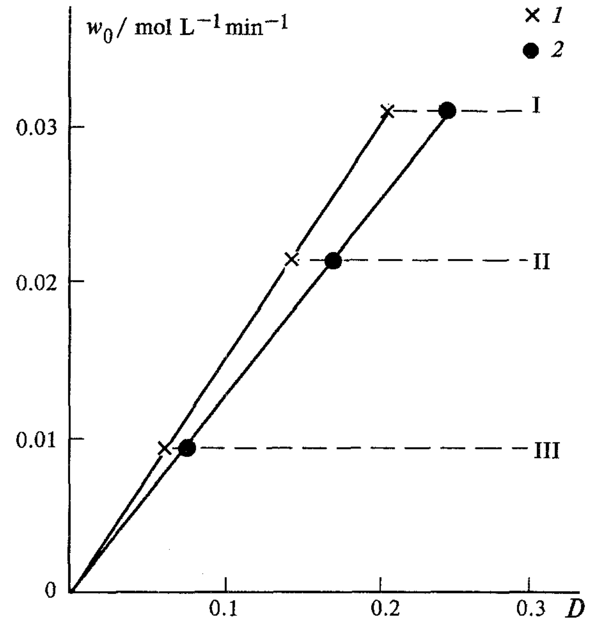

**Fig. 2.** Dependence of the initial rate of the hydroformylation of $CH_2O$ ($w_0$) on the optical densities ($D$) of the absorption bands at 1990 cm$^{-1}$ (*1*) and 1932 cm$^{-1}$ (*2*) that are proportional to the initial concentration of the $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ anion formed from $RhCl(PPh_3)_3$ (I), $RhH(CO)(PPh_3)_3$ (II), or $RhCl(PPh_3)_3$ + 10 $PPh_3$ (III) under the reaction conditions.

confirms that ionic structures participate in the hydroformylation of $CH_2O$.

In the presence of $PPh_3$-containing Rh complexes, the limiting step of reaction (1) is probably the interaction of $CH_2O$ with the rhodium site: (1) the reaction has the first order with respect to $CH_2O$ and Rh (Fig. 3, *b*, *c*) and also with respect to anionic complex $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (see Fig. 2); (2) the IR spectra recorded under the conditions of the hydroformylation in the presence and in the absence of aldehyde are identical. Taking the foregoing into account, one may attribute the increase in the rate of the hydroformylation of $CH_2O$ with increase in the concentration of the anionic carbonylrhodium complex (see Fig. 2) or with increase in the concentration of protons (see Fig. 3, *a*) to the fact that ionic structures participate in the hydroformylation of $CH_2O$ during the activation of the aldehyde, which can be hypothetically described in the following way:

$$CH_2O + H^+ + [Rh(CO)_2(PPh_3)_x(DMAA)_y]^- \rightarrow$$
$$\rightarrow HOCH_2Rh(CO)_2(PPh_3)_x(DMAA)_y.$$

## References

1. A. J. Spencer, *J. Organomet. Chem.*, 1980, **194**, 113.
2. S. E. Jacobson, *J. Mol. Catal.*, 1987, **41**, 163.
3. L. C. Costa, *Catal. Rev.-Sci. Eng.*, 1983, **25**, 325.
4. A. S. C. Chan, W. E. Carrol, and D. E. Willis, *J. Mol. Catal.*, 1983, **19**, 377.
5. M. Marchionna and G. Longoni, *Organometallics*, 1987, **6**, 606.
6. M. Marchionna, Z. Garlaschelli, and J. Longoni, *J. Mol. Catal.*, 1989, **57**, 221.
7. USSR Pat. 1698713, *Byul. Izobret.*, 1986, 13 (in Russian).
8. G. A. Korneeva, N. N. Ezhova, V. G. Avakyan, E. V. Slivinskii, and S. M. Loktev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2670 [*Bull. Acad. Sci USSR, Div. Chem. Sci.*, 1989, **38**, 2444 (Engl. Transl.)].
9. G. Wilkinson, J. A. Osborn, F. H. Jardine, and J. F. Young, *J. Chem. Soc.*, A, 1966, **12**, 171.
10. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.*, A, 1969, **11**, 2660.

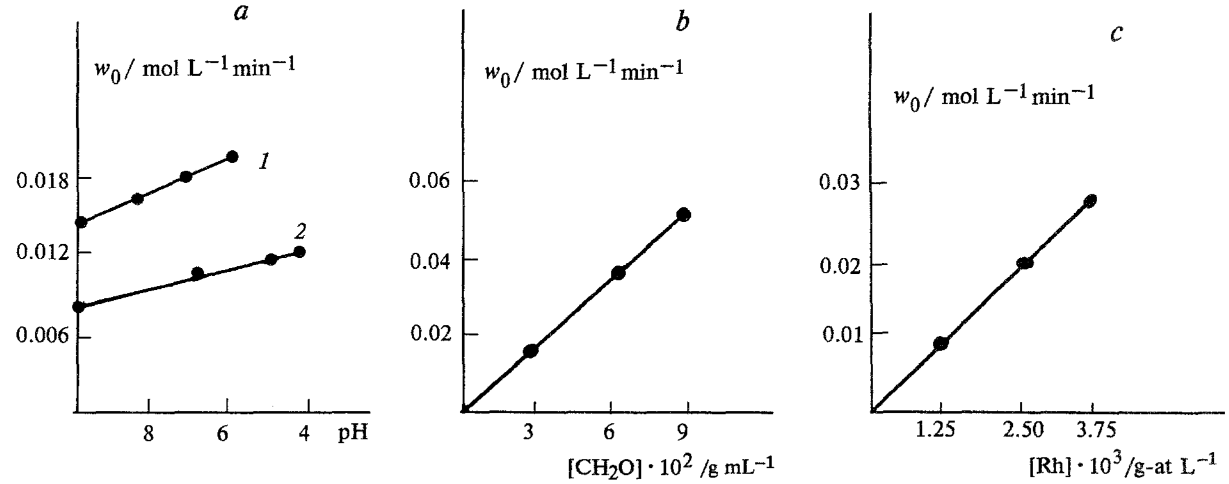

**Fig. 3.** Effects of various factors on the initial rate of the hydroformylation of $CH_2O$: *a* — pH of the reaction solution (*1*, $RhCl(PPh_3)_3$, [Rh] = $2.5 \cdot 10^{-3}$ g-at L$^{-1}$, $[H_2O]$ = 1.3 mol L$^{-1}$, $CH_3COOH$; *2*, $RhH(CO)(PPh_3)_3$, [Rh] = $2.5 \cdot 10^{-3}$ g-at L$^{-1}$, $[H_2O]$ = 0.9 mol L$^{-1}$, HCl), *b* — initial concentration of formaldehyde ($RhCl(PPh_3)_3$, [Rh] = $2.5 \cdot 10^{-3}$ g-at L$^{-1}$), *c* — concentration of $RhCl(PPh_3)_3$, $[CH_2O]_0$ = 0.03 g mL$^{-1}$ ($T$ = 383 K, $p_{1CO:1H}$ = 13 MPa, 60 mL of DMAA).

11. N. Armed, S. D. Robinson, and M. F. Utten, *J. Am. Chem. Soc.*, 1972, **27**, 389.
12. Yu. S. Varshavskii and T. G. Cherkasova, *Zh. Neorg. Khim.*, 1967, **12**, 1709 [*J. Inorg. Chem. USSR*, 1967, **12** (Engl. Transl.)].
13. S. Martinengo, P. Chini, and G. Giodano, *J. Organomet. Chem.*, 1971, **276**, 389.
14. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.*, A, 1968, **11**, 2660.
15. W. R. Moser, C. J. Papile, D. A. Brannon, and R. A. Duwell, *J. Mol. Catal.*, 1987, **41**, 271.
16. J. P. Collman, F. D. Vastine, and W. Roper, *J. Am. Chem. Soc.*, 1968, **90**, 2282.
17. Yu. B. Kagan, G. A. Korneeva, O. L. Butkova, M. V. Shishkina, and A. N. Bashkirov, *Neftekhimiya* [*Petrochemistry*], 1982, **22**, 345 (in Russian).
18. A. Fumagalli, T. F. Koetzle, and F. Takusagawa, *J. Am. Chem. Soc.*, 1980, **10**, 1740.

*Received July 7, 1994;*
*in revised form December 22, 1994*