Transformation of rhodium carbonyl complexes in hydroformylation of 1-hexene studied from *in situ* IR spectroscopic data

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Rhodium carbonyl complexes that formed from $RhCl_3 \cdot 4H_2O$ and $RhCl_3 \cdot 4H_2O$ modified by poly-*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride in a methanol—chloroform medium in the hydroformylation of 1-hexene were studied by *in situ* IR spectroscopy. Along with the rhodium hydrocarbonyl complexes, anionic complexes of the $[Rh(CO)_2Cl_2]^-$ type, whose concentrations and rates of formation in an acidic medium are much higher than those in a basic medium, were shown to be the active centers of hydroformylation. The function of the polycation is the stabilization of the catalytically active mononuclear rhodium complexes.

Key words: hydroformylation, 1-hexene, rhodium catalysts, polycations.

Studies of the mechanism of hydroformylation reactions under conditions of phase-transfer catalysis involve experimental difficulties caused by the presence of two immiscible phases, one of which is water, the problem of solubility of the components, and others.[1–3] The study of the composition and structure of the catalytically active complexes that form in water is not of theoretical interest only, but it also allows one to develop basically new approaches to improvement of catalysts of hydroformylation under these conditions.

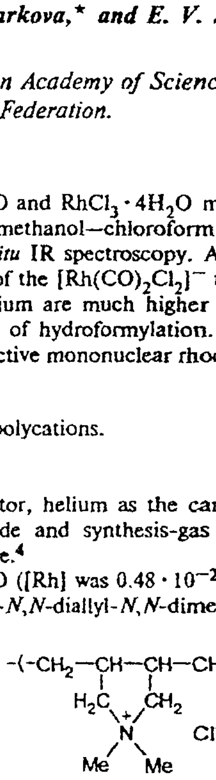
In this work, we carried out *in situ* IR spectroscopic study of the formation of carbonyl complexes from $RhCl_3 \cdot 4H_2O$ and Rh^{III} chloride modified by the water-soluble polycation (WPC) poly-*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride in a methanol—chloroform medium under conditions of 1-hexene hydroformylation.

Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer in the 2100—1700 cm^{-1} region with a resolution of ±2 cm^{-1} and an integration time of 1 s. The spectra were recorded with the compensation of absorption of the solvent and dissolved CO. A cell-autoclave placed directly in the cell compartment of the spectrometer was used in experiments. The windows of the cell were made of a CaF_2 single crystal. The layer thickness in the IR-cell was ~300 μm. All spectra were recorded under anaerobic conditions at 60±1 °C and a synthesis-gas pressure of 6.0 MPa. Hydroformylation of 1-hexene was carried out directly in the IR-cell at $T = 60$ °C, $p = 6.0$ MPa (CO : H_2 = 1), recording the spectra at specified intervals.

The reaction products were analyzed on a Chrom-5 chromatograph (a capillary column 25 m long, PEG-20M, a flame-ionization detector, helium as the carrier gas, $T = 120$ °C). Carbon monoxide and synthesis-gas were obtained by the known procedure.[4]

$RhCl_3 \cdot 4H_2O$ ([Rh] was $0.48 \cdot 10^{-2}$ g-at. L^{-1} in all experiments) and poly-*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride



were used as the components of the catalytic system. The molecular weight of WPC was 30000. The Rh : WPC molar ratio was 0.13 in all experiments.

The $RhCl_3$—WPC complex was prepared at atmospheric pressure and room temperature, pH of the solution being 5—5.5.

Results and Discussion

The study of transformations of $RhCl_3 \cdot 4H_2O$ in the synthesis-gas atmosphere at pH 4—5 in the starting solution (Fig. 1) in the absence of olefin showed that at the initial moment the spectrum contains absorption bands at 2076, 2044, and 1884 cm^{-1} attributed[5] to $Rh_4(CO)_{12}$, a band at 1812 cm^{-1} characterizing[6] $Rh_6(CO)_{16}$, and bands at 2002 cm^{-1} and 2056 cm^{-1} that can be assigned to $[Rh(CO)_2Cl_2]$ [1] (see Fig. 1, *a*). Absorption bands at 2076 and 2044 cm^{-1} can also be assigned to rhodium hydrocarbonyl $HRh(CO)_4$, which, as is known,[5] is in equilibrium with $Rh_4(CO)_{12}$ in the synthesis-gas atmosphere. After a solution of the complex was exposed to the synthesis-gas atmosphere for 10 min, in the IR spectrum (see Fig. 1, *b*) the intensities

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of all absorption bands increase and additional bands appear at 2012, 1870, and 1848 cm^{-1}, which can be attributed to the polynuclear anionic rhodium complex $[Rh_5(CO)_{15}]^-$.[1] The disappearance of the band at 1884 cm^{-1} corresponding to vibrations of bridging carbonyl groups of the $Rh_4(CO)_{12}$ cluster indicates that dodecacarbonyltetrarhodium is transformed into $HRh(CO)_4$ under the action of the synthesis-gas. As the time of exposure of the solution to the synthesis-gas atmosphere increases, a greater increase in intensities is observed for all absorption bands except for the band at 2076 cm^{-1}, whose intensity decreases (see Fig. 1, *c*). Thus, a long exposure of the rhodium complexes to the synthesis-gas medium results in the accumulation of anionic mono- and polynuclear forms, as well as neutral carbonyl $Rh_6(CO)_{16}$.

For the hydroformylation of 1-hexene (Fig. 2, *a*) in the presence of $RhCl_3 \cdot 4H_2O$, bands attributed to $HRh(CO)_4$ (2076, 2044 cm^{-1}),[5] $[Rh_5(CO)_{15}]^-$ (2012 cm^{-1}),[1] and rhodium acylcarbonyl complex (2044, 2112 cm^{-1})[7] are observed in the spectrum at the initial moment. Twenty min later (Fig. 2, *b*), the intensity of the band at 2076 cm^{-1} decreases sharply, the intensity of the band at 2044 cm^{-1} increases, and that of the band at 2012 cm^{-1} remains unchanged.

The hydroformylation of 1-hexene reaches a stationary regime with time, and the ratio of intensities of all bands in the IR spectrum is stabilized. As 1-hexene is consumed and the hydroformylation reaction decays, the intensity of the band at 2044 cm^{-1} decreases and those of the bands at 2076 and 2012 cm^{-1} increase, *i.e.*, the acyl form is transformed into two carbonyl forms, $HRh(CO)_4$ and $[Rh_5(CO)_{15}]^-$.

Based on the data obtained, we conclude that three compounds — the acylcarbonyl complex (predominantly), the neutral complex $HRh(CO)_4$, and the anionic cluster $[Rh_5(CO)_{15}]^-$ — are formed from the starting salt $RhCl_3 \cdot 4H_2O$ under conditions of hydroformylation in a methanol—chloroform mixture. As 1-hexene is consumed, the concentrations of acyl forms of rhodium decrease and the content of complexes, which do not participate in the catalytic cycle of hydroformylation, increases simultaneously.

Thus, the anionic mononuclear rhodium carbonyl complexes are readily transformed into acyl complexes rather than the present products of decomposition of the latter.

Then we studied the transformations of the $RhCl_3 \cdot$WPC complex in a methanol—chloroform medium under the action of the synthesis-gas in the absence of olefin ("blank experiment").

At the initial moment (Fig. 3, *a*), the IR spectrum exhibits absorption bands corresponding to the neutral $HRh(CO)_4$ (2076, 2044 cm^{-1}) and anionic $[Rh(CO)_2Cl_2]^-$ (2002 and 2056 cm^{-1}) rhodium carbonyl complexes, and the latter dominates in the solution. At a longer exposure to a CO/H_2 mixture (Fig. 3, *b*), the intensities of these bands increase and change insignificantly during the next 2 h (Fig. 3, *c*).

The absence of bands characteristic of vibrations of bridging carbonyl groups of the cluster anionic and neutral rhodium complexes suggests that the polycationic ligand stabilizes the neutral and anionic mononuclear rhodium complexes and prevents the formation of clusters.

It was of interest to monitor the influence of the pH of the solution on the formation of the rhodium carbonyl complexes during treatment of the $RhCl_3 \cdot$WPC system with synthesis-gas in the absence of olefin. For this purpose, the pH of the starting solution of $RhCl_3 \cdot$WPC was increased to 7—8 at the stage of its preparation by addition of a 0.1 *M* solution of KOH.

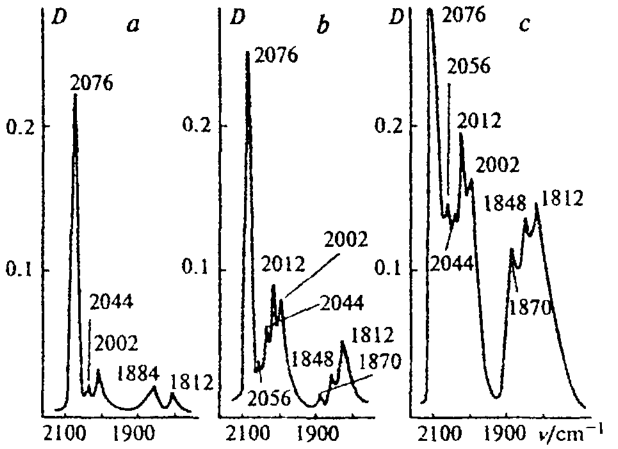

Fig. 1. IR spectra of a solution of $RhCl_3 \cdot 4H_2O$ in the synthesis-gas medium for 2 (*a*), 10 (*b*), and 60 min (*c*). T = 60 °C, p_{CO+H_2} = 6 MPa, [Rh] = $0.48 \cdot 10^{-2}$ g-at. L^{-1}, methanol—chloroform (3 : 7, v/v) as the solvent, pH 4—5.

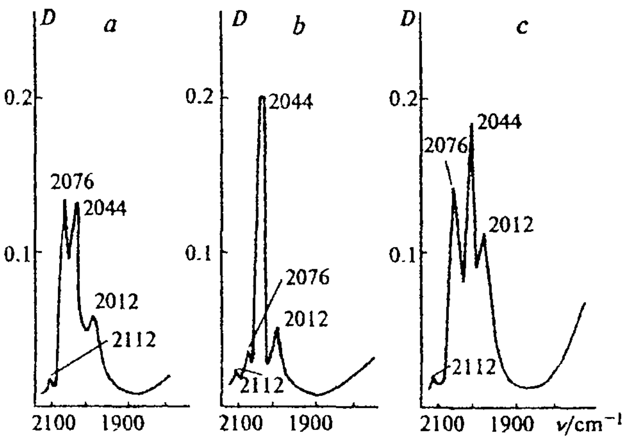

Fig. 2. IR spectra of a solution of $RhCl_3 \cdot 4H_2O$ under conditions of 1-hexene hydroformylation for 10 (*a*), 20 (*b*), and 120 min (*c*). T = 60 °C, p_{CO+H_2} = 6 MPa, [Rh] = $0.48 \cdot 10^{-2}$ g-at. L^{-1}, $[C_6H_{12}]$ = 0.8 mol L^{-1}, 10 mL of methanol—chloroform (3 : 7, v/v).

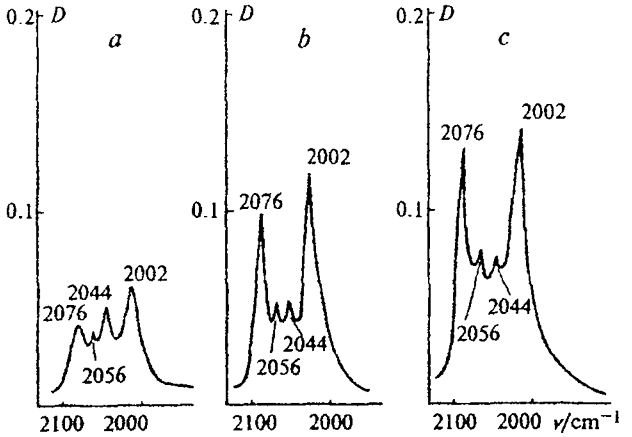

Fig. 3. IR spectra of a solution of $RhCl_3 \cdot WPC$ in the synthesis-gas medium for 2 (*a*), 10 (*b*), and 60 min (*c*). $T = 60$ °C, $p_{CO+H_2} = 6$ MPa, $[Rh] = 0.48 \cdot 10^{-2}$ g-at. L^{-1}, methanol—chloroform (3 : 7, v/v) as the solvent, starting solution pH 5—5.5.

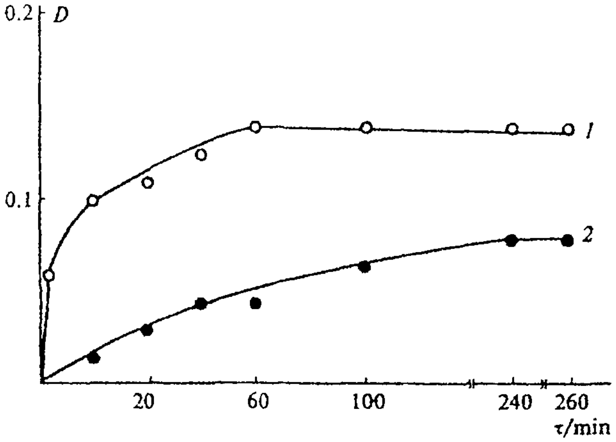

Fig. 4. Changes in the optical density (*D*) of the absorption band at 2002 cm^{-1} in time at pH 5—5.5 (*1*) and 7—8 (*2*) during treatment of $RhCl_3 \cdot WPC$ with the synthesis-gas. $T = 60$ °C, $p = 6$ MPa, $CO : H_2 = 1$, $[Rh] = 0.48 \cdot 10^{-2}$ g-at. L^{-1}, methanol—chloroform (3 : 7, v/v).

Preliminary experiments showed that the presence of K^+ ions in the system has no effect on the catalytic properties of the $RhCl_3 \cdot WPC$-based complexes.

It was established that an increase in pH did not result in a change in the composition of the rhodium carbonyl complexes that formed: the series of absorption bands remained the same, and their intensity also increased in time.

The change in the optical density (*D*) of the absorption band at 2002 cm^{-1} during treatment of a solution of $RhCl_3 \cdot WPC$ with the synthesis-gas under hydroformylation conditions in the absence of olefin at pH 5—5.5 and 7—8 of the starting solution of $RhCl_3 \cdot WPC$ is presented in Fig. 4.

In an acidic medium, the concentration and rates of formation of the anionic mononuclear complexes are much higher than those in an alkaline medium: at pH 5—5.5, their formation is ceased in 1 h, whereas at pH 7—8, this requires 4 h.

Thus, under conditions of biphase catalysis with a polar solvent as one of the phases, rhodium hydrocarbonyl complexes and anionic complexes participating in olefin hydroformylation can be formed. The addition of the polycation to the catalytic system stabilizes the catalytically active complexes, preventing their aggregation, and forming clusters inactive in the hydroformylation.

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