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Homogeneous Rhodium–Copper–Halide Catalytic Systems for the Oxidation and Oxidative Carbonylation of Methane

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Abstract—Homogeneous catalytic systems for the oxidation and oxidative carbonylation of methane in aqueous trifluoroacetic acid solutions were developed. The system included rhodium compounds and copper compounds as cocatalysts. Methanol, methyl trifluoroacetate, formic acid, and acetic acid were the reaction products. The process was accompanied by the intense oxidation of CO to CO_2. Regularities of the process were studied, optimum process parameters were determined, and conditions at which methyl trifluoroacetate was formed with ~90% selectivity were found. Kinetic isotope effects with respect to the solvent were determined. For the formation of organic products, k_H/k_D was ~1, whereas it was ~1.6 for the oxidation of CO. Studies were also performed with the use of compounds containing the ^{18}O isotope. Conceivable mechanistic models of this process are discussed.

INTRODUCTION

The catalytic functionalization of methane and its homologues is one of the most important problems of modern chemistry [1–12]. The partial oxidation and oxidative carbonylation of methane are thermodynamically sound reactions. As stated in an analytical report of the Network for Industrial Catalysis in Europe, the direct conversion of methane into methanol with high activity and selectivity remains an important problem that should be solved [13].

Metal complex systems for methane activation, oxidation, and oxidative carbonylation in protic media are known (see, for example, [14–28]). Moiseev and coworkers found that direct interaction between oxidizing and reducing agents is not necessary in redox reactions. A catalytic cycle can be constructed by coupling stoichiometric reactions; this was successfully accomplished in the oxidation of ethylene in the Pd(II)–cocatalyst–O_2 system. Compounds prone to easy redox transitions, such as quinones and $CuCl_2$, were used as cocatalysts [4]. This approach was practically implemented in the construction of the rhodium–iodide–chloride system for the oxidation and oxidative carbonylation of methane in the presence of molecular oxygen and carbon monoxide [25–28]. The volatility and corrosion activity of iodine compounds restrict their use as cocatalysts. Because of this, we performed preliminary studies in order to find iodide-free catalytic systems for the oxidation and oxidative carbonylation of methane. We found that, as reported previously [29, 30], the compounds of copper and iron are effective as cocatalysts.

In this work, we consider in more detail the catalytic properties of the rhodium–copper–chloride system in the oxidation and oxidative carbonylation of methane in the presence of O_2 and CO and some mechanistic aspects of these reactions.

EXPERIMENTAL

The following chemicals were used in this study: $RhCl_3 \cdot (H_2O)_n$ (34.5 wt % Rh), NaCl, NaBr, KI, CuO, and Cu_2O (chemically pure); C_2H_5COOH (chemically pure); H_2O (twice distilled); D_2O (99.9% D); CF_3COOD (99.9% D); and $H_2{}^{18}O$ (80.1% ^{18}O). CF_3COOH was distilled in the presence of concentrated H_2SO_4; $CF_3C^{16}O^{18}OH$ (20% ^{18}O) was prepared by carefully mixing freshly prepared trifluoroacetic anhydride with an equimolar amount of $H_2{}^{18}O$. The purity of gases was as follows: CH_4 99.8%; CO, 99.9%; O_2, 99.5%; and $^{18}O_2$, 60.1% ^{18}O. The complexes of Rh, Ru, Pt, and Pd were synthesized in accordance with well-known procedures.

The catalytic experiments were performed in a 34-cm^3 stainless-steel reactor lined with fluoroplastic. The contact between a liquid phase and the metal was completely precluded, whereas the contact of a vapor–gas phase with the metal was reduced to a minimum in the nonheated part. A solution of $RhCl_3$ in H_2O or D_2O, NaCl, and a corresponding cocatalyst (Cu_2O or CuO) were placed in the reactor; then, CF_3COOH or CF_3COOD was added. To accurately maintain the ratio between water and trifluoroacetic acid, the catalytic system was prepared by weighing all components, including liquids, in a special container. The total volume of a liquid phase was 2.5 cm^3. A fluoroplastic disk was plunged into the reactor, which was hermetically sealed and connected to a gas-mixing unit equipped with a reference pressure gauge of 10 MPa (graduated to 0.04 MPa). In standard experiments, CH_4 (6 MPa),

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O_2 (0.56 MPa), and CO (1.84 MPa) were fed in the specified sequence. On varying the ratio between gases, preliminary calculations were performed to avoid the formation of explosive mixtures. The jacket of the reactor was connected to a water ultrathermostat preheated to an experiment temperature (95°C). The experiments were performed with the intense stirring of gaseous and liquid phases using a shaker. After completion of an experiment, the reactor was rapidly cooled to 12°C; a gas phase was collected for analysis, and a liquid phase was quantitatively frozen before analysis.

The gas phase was analyzed on a Model 3700 chromatograph (Khromatograf Moscow Pilot Plant) equipped with a 3-m column packed with molecular sieves 5 Å (O_2, N_2, CH_4, and CO) and a 2-m column packed with Porapak Q (CO_2 and organic products). A thermal-conductivity detector was used; helium was a carrier gas. Gases were analyzed at 55°C with an accuracy of 10%. The liquid phase was analyzed at 165°C; propionic acid was used as an internal standard. The accuracy of analysis was 10–15%. In the experiments with tracer elements, the purity of initial gases and the isotope composition of methane and CO_2 were determined by mass spectrometry on an MI-1201 instrument.

PRINCIPLES OF CONSTRUCTING CATALYTIC SYSTEMS

Methane conversion was not observed in early experiments performed in the $RhCl_3$–Cu(II)–Cl^- system in aqueous trifluoroacetic acid without CO and O_2. The addition of CO resulted in its intense oxidation to CO_2; methane reaction products were also absent. The oxidation and oxidative carbonylation of methane took place only in the system containing both CO and O_2. Thus, the role of Cu(II) in the test reactions is not so simple as that in the oxidation of olefins and CO in the presence of platinum-group metal complexes.

Data obtained in studies of the rhodium–iodide–chloride catalytic system [25–28] made it possible to formulate the general requirements imposed on cocatalysts. First, the cocatalysts should be prone to easy redox transitions. Next, the reduced forms of the cocatalysts should react with molecular oxygen to form two-electron oxidizing agents, such as hypoiodous acid and hydrogen peroxide. In rhodium complex catalysis, the reduced forms should be regenerated under the action of carbon monoxide on the oxidized forms. In accordance with this, we believe that, in the $RhCl_3$–KI–NaCl system in an acidic medium, intermediate oxidizing agents are formed in the following reactions [31]:

$$2HI + O_2 \longrightarrow 2HOI, \qquad \text{(I)}$$

$$2HI + O_2 \longrightarrow H_2O_2 + I_2. \qquad \text{(II)}$$

Undoubtedly, the following reactions are also effective:

$$2HI + 1/2O_2 \longrightarrow I_2 + H_2O, \qquad \text{(III)}$$

$$CO + HOI(H_2O_2) \xrightarrow{Rh} CO_2 + HI(H_2O). \qquad \text{(IV)}$$

In catalysis with the carbonyl–halide complexes of rhodium(I), the reduced form is regenerated by the reaction

$$I_2 + CO + H_2O \xrightarrow{Rh} 2HI + CO_2. \qquad \text{(V)}$$

In the newly developed iodide-free catalytic system, the formation of hydrogen peroxide and the regeneration of the reduced form of the cocatalyst take place in the reactions [32]

$$2Cu^+ + 2H^+ + O_2 \longrightarrow 2Cu^{2+} + H_2O_2, \qquad \text{(VI)}$$

$$2Cu^{2+} + CO + H_2O \xrightarrow{Rh} 2Cu^+ + CO_2 + 2H^+. \qquad \text{(VII)}$$

It is probable that free hydrogen peroxide is not released, but copper hydroperoxide is formed in the reaction

$$2CuCl + O_2 + H^+ \longrightarrow CuCl\text{–}OOH + CuCl^+. \qquad \text{(VIII)}$$

RESULTS

Copper as oxides was introduced into the rhodium–copper–chloride catalytic system. This was done for experimental convenience and because of a necessity for studying the process at low concentrations of chloride ions. Previously, we found that copper oxides are rapidly dissolved in a mixture of CF_3COOH and H_2O, especially, in the presence of CO. The salts of Cu(I) are best soluble in the presence of an excess of halide ions. However, at the ratio Cl/Cu = 5–1, the products were detected only in trace amounts. As follows from Table 1, the catalytic activity appears at the ratio Cu/Cl > 1. At a constant concentration of copper, a small maximum of the yield of products was observed as the concentration of chloride ions was decreased (experiment nos. 1–3). However, the yield noticeably increased as the concentration of copper was decreased by a factor of 2 (experiment no. 4). If the concentration of chloride ions was also then decreased, the yield of products remained almost unchanged (experiment no. 5). The ratio between components of the catalytic system close to an optimum value was observed in experiment no. 6. The results of experiment nos. 7 and 8 suggest that a further decrease in the concentrations of copper and chloride ions decreased the yield of products. The initial oxidation state of copper (experiment nos. 9, 10), as well as a twofold change in the concentrations of all components except for acetic acid (experiment nos. 6, 9), had almost no effect on the yield of products. Thus, the effects of the concentrations of copper and chloride ions are complicated and interdependent. The quantitative description of the process would be possible upon measuring the constants of equilibrium between free chloride ions and the chloride complexes of rhodium under conditions of the experiments.

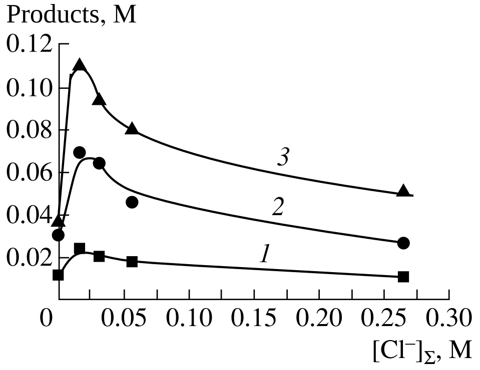


Fig. 1. Yields of products of the reaction of CH_4, CO, and O_2 at 95°C as functions of the concentration of chloride ions: (*1*) HCOOH, (*2*) CH_3COOH, and (*3*) CF_3COOCH_3. $CF_3COOH–H_2O$, m_{H_2O} = 0.67; $[RhCl_3] = 5 \times 10^{-3}$ M; [Cu(I)] = 0.2 g-ion/l. Initial pressures (at T_{room}), MPa: CH_4, 6.00; CO, 1.84; and O_2, 0.56. In the experiment at $[Cl^-] = 0$, $Rh(acac)(CO)_2$ was used.

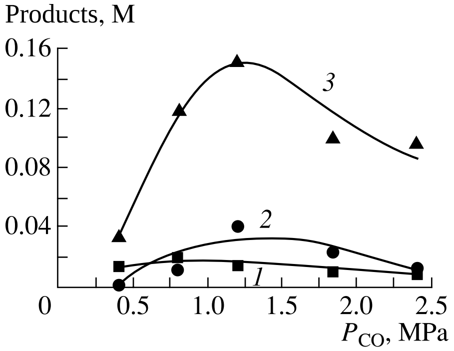


Fig. 2. Yields of products of the reaction of CH_4, CO, and O_2 at 95°C as functions of CO pressure: (*1*) HCOOH, (*2*) CH_3COOH, and (*3*) CF_3COOCH_3. $CF_3COOH–H_2O$, m_{H_2O} = 0.62; $[RhCl_3] = 2.5 \times 10^{-3}$ M; $[Cu(II)] = 5 \times 10^{-2}$ g-ion/l; $[NaCl] = 1.5 \times 10^{-2}$ M. Initial pressures (at T_{room}), MPa: CH_4, 6.00 and O_2, 0.56.

Regularities of the process were studied. Figure 1 demonstrates the yields of products as functions of chloride ion concentration. A sharp maximum is observed in the initial portion; then, the yield monotonically decreases. Extremal functions were also observed on varying the pressure of CO (Fig. 2). We relate the decrease of product yields (Figs. 1, 2) to the inhibition of the formation of a catalytically active intermediate (a coordinatively unsaturated rhodium complex) as the concentration of chloride ions and the pressure of CO were increased over optimum values. The dependence of the yield of reaction products on water concentration (Fig. 3) is characterized by broad maximums for methyl trifluoroacetate and acetic acid. Thus, the catalytic system under study is much less sensitive to water than the rhodium–iodide–chloride sys-

Table 1. Yields of products of the oxidation and oxidative carbonylation of methane in the presence of the $RhCl_3$–Cu(I, II)–NaCl catalytic system in a $CF_3COOH–H_2O$ medium at m_{H_2O} = 0.62 depending on the ratio between components*

Experiment no.	[Cu(II)], g-ion/l	$[NaCl] \times 10^2$, M	Rh(III) : Cu(II) : Cl^-_Σ	$[CF_3COOCH_3]$ + $[CH_3OH]$, M	$[CH_3OOH]$, M	[HCOOH], M
1	0.200	5.25	1 : 80 : 24	0.044	0.010	<0.005
2	0.200	3.00	1 : 80 : 15	0.110	0.034	0.010
3	0.200	1.50	1 : 80 : 9	0.077	0.030	0.010
4	0.100	1.50	1 : 40 : 9	0.137	0.042	0.015
5	0.100	0.75	1 : 40 : 6	0.132	0.030	0.007
6	0.050	0.75	1 : 20 : 6	0.170	0.035	0.020
7	0.025	0.75	1 : 10 : 6	0.056	0.010	0.003
8	0.025	0.25	1 : 10 : 4	0.037	0.006	0.003
9**	0.100	1.50	1 : 20 : 6	0.168	0.075	0.020
10***	0.100	1.50	1 : 20 : 6	0.140	0.067	0.020

* The reaction was performed to a residual O_2 content of ~0.6–1.0 vol % at 95°C. The initial reactant pressures at T_{room} were as follows (MPa): CH_4, 6.00; CO, 1.84; and O_2, 0.56, $[RhCl_3] = 2.5 \times 10^{-3}$ M.

** $[RhCl_3] = 5 \times 10^{-3}$ M.

*** $[RhCl_3] = 5 \times 10^{-3}$ M; Cu_2O.

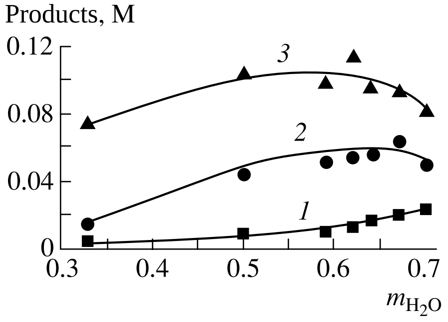


Fig. 3. Yields of products of the reaction of CH_4, CO, and O_2 at 95°C as functions of the mole fraction of water in CF_3COOH solutions: (*1*) HCOOH, (*2*) CH_3COOH, and (*3*) CF_3COOCH_3. $[RhCl_3] = 5 \times 10^{-3}$ M; [Cu(I)] = 0.2 g-ion/l; $[NaCl] = 1.5 \times 10^{-2}$ M. Initial pressures (at T_{room}), MPa: CH_4, 6.00; CO, 1.84; and O_2, 0.56.

tem [25–28]. Reasonably high selectivity (~90%) to methyl trifluoroacetate can be attained under certain conditions (a low concentration of water and moderate degrees of O_2 conversion). It is well known that this product can be easily saponified.

Figures 4 and 5 demonstrate the kinetic curves of the oxidation and oxidative carbonylation of methane in $CF_3COOH–H_2O$ and $CF_3COOD–D_2O$ at a mole fraction of water, *m*, equal to 0.62. It follows that the kinetic isotope effect (KIE) k_H/k_D with respect to the solvent in the formation of organic products is close to 1. At the same time, KIE is ~1.6 in the oxidation of CO to CO_2 under the same conditions.

The dissolution of titanium metal is a test for the formation of two-electron oxidizing agents (H_2O_2)) from O_2 [28]. Table 2 indicates that, as well as the yields of methyl trifluoroacetate and acetic acid, the intensity of titanium dissolution ($\Delta Ti/t$) in the test system as a function of water concentration passes through a maximum. Thus, it is believed that both methane and titanium were oxidized under the action of the same agent—H_2O_2.

It was of importance to determine from which reactant the oxygen atom was incorporated into products. We succeeded in determining this for only CO_2. We used the ^{18}O isotope in the compounds $^{18}O_2$, $H_2{}^{18}O$, and $CF_3CO^{18}OH$. We found in preliminary experiments that oxygen atom exchange between the CO_2 molecule and the medium is insignificant. We found that in the oxidation of CO in the standard catalytic system (Table 1, experiment no. 6) ~15% oxygen atoms entered into CO_2 from molecular oxygen, ~13% from water, and ~54% from CF_3COOH.

We found that HCOOH was stable under the experimental conditions, and it was not oxidized into CO_2. The decarboxylation of CF_3COOH was not detected, as evidenced by the total absence of CF_3H from the reaction products. The total CO_2 resulted from the oxidation of CO; this is consistent with a satisfactory material balance. The addition of inhibitors (chloranil and ionol) had no effect on the course of the process.

DISCUSSION

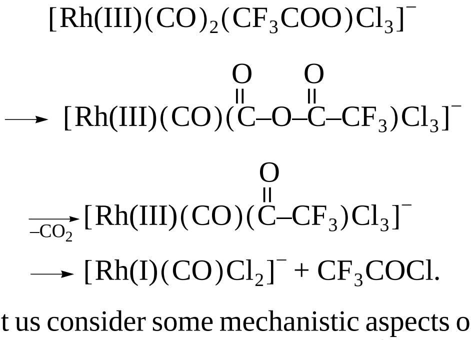
In both the system under study and the rhodium–iodide–chloride system, KIE > 1 for CO oxidation. This is due to the equilibrium deprotonation of an aqua carbonyl complex of Rh(III) [33] by the reaction

$$\begin{aligned}&[\mathrm{Rh(CO)_2(H_2O)Cl_3}]\\ &\longleftrightarrow [\mathrm{Rh(CO)_2(OH)Cl_3}]^- + \mathrm{H}^+.\end{aligned} \qquad \text{(IX)}$$

The $[Rh(CO)_2(H_2O)Cl_3]$ complex is a weak acid, and the dissociation constants of weak acids in D_2O are lower than those in H_2O by a factor of 2 to 3 [34]. If KIE > 1 with respect to solvent, a step of H (D)–element bond dissociation occurred, which either preceded the first irreversible step or was the first irreversible step. Otherwise, KIE may be ~1 or <1. At least the following three examples provide support for this statement: the oxidation of ethylene to acetaldehyde in the presence of palladium chlorides, KIE ~4 [35]; the water-gas shift reaction on the phosphine complexes of palladium in aqueous CF_3COOH, KIE ~3 [36]; and the oxidative carbonylation of acetylene, KIE = 1.7–1.8 [37].

In this context, it is believed that the values of KIE (~1 for the formation of organic products in the rhodium–copper–chloride system and ~2 in the rhodium–iodide–chloride system) can be explained as described below. The formation of H_2O_2 by reaction (VI) is not accompanied by H–element bond dissociation. At the same time, in the iodide system, H–I bond dissociation (reactions (I) and (II)) is required for the generation of two-electron oxidizing agents.

Reaction sequence (X) explains how the oxygen atom from CF_3COOH enters into CO_2. A coordinatively unsaturated Rh(I) complex is an intermediate in the oxidation of CO.



$$\begin{aligned}&[\mathrm{Rh(III)(CO)_2(CF_3COO)Cl_3}]^-\\ &\longrightarrow [\mathrm{Rh(III)(CO)}(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{–O–}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{–CF_3})\mathrm{Cl_3}]^-\\ &\xrightarrow[-\mathrm{CO_2}]{} [\mathrm{Rh(III)(CO)}(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{–CF_3})\mathrm{Cl_3}]^-\\ &\longrightarrow [\mathrm{Rh(I)(CO)Cl_2}]^- + \mathrm{CF_3COCl}.\end{aligned} \qquad \text{(X)}$$

Let us consider some mechanistic aspects of the oxidation and oxidative carbonylation of methane in the presence of rhodium systems. According to our findings and published data [38], a radical mechanism is highly improbable. In the rhodium–iodide–chloride system, the formation of CH_3I and its oxidative addition to Rh(I) do not occur. According to Lin *et al.* [38], the yields of methane and acetic acid depend on the ratio

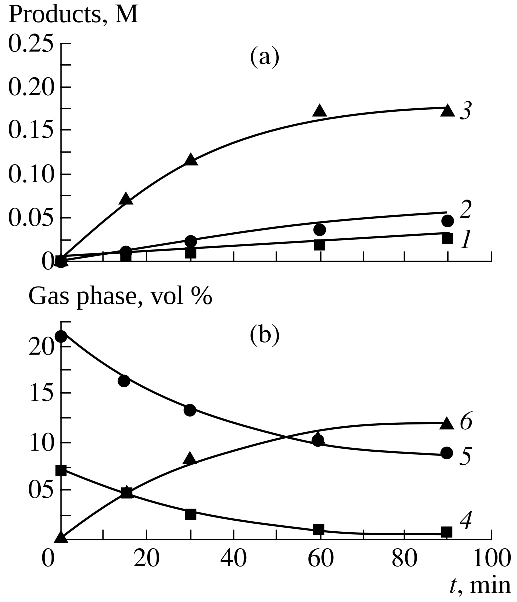


Fig. 4. The time dependence of the composition of (a) gas and (b) liquid phases in the reaction of CH_4, CO, and O_2 at 95°C: (*1*) HCOOH, (*2*) CH_3COOH, (*3*) CF_3COOCH_3, (*4*) O_2, (*5*) CO, and (*6*) CO_2. $CF_3COOH–H_2O$, m_{H_2O} = 0.62; $[RhCl_3] = 2.5 \times 10^{-3}$ M; [Cu(II)] = 5×10^{-2} g-ion/l; [NaCl] = 1.5×10^{-2} M. Initial pressures (at T_{room}), MPa: CH_4, 6.00; CO, 1.84; and O_2, 0.56.

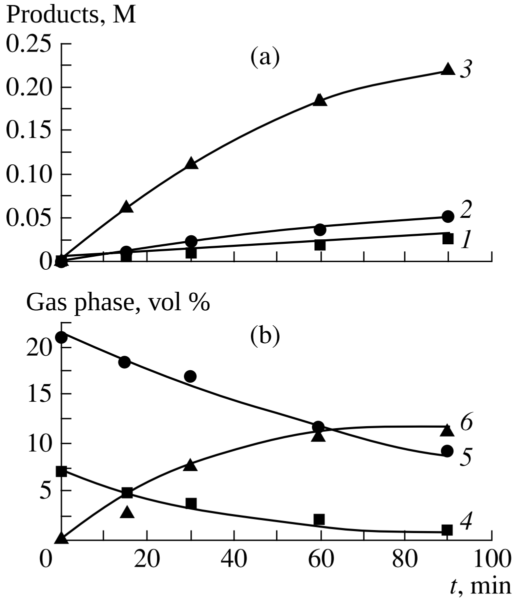


Fig. 5. The time dependence of the composition of (a) gas and (b) liquid phases in the reaction of CH_4, CO, and O_2 at 95°C: (*1*) HCOOD, (*2*) CH_3COOD, (*3*) CF_3COOCH_3, (*4*) O_2, (*5*) CO, and (*6*) CO_2. $CF_3COOD–D_2O$, m_{D_2O} = 0.62; $[RhCl_3] = 2.5 \times 10^{-3}$ M; [Cu(II)] = 5×10^{-2} g-ion/l; [NaCl] = 1.5×10^{-2} M. Initial pressures (at T_{room}), MPa: CH_4, 6.00; CO, 1.84; and O_2, 0.56.

between the rate constants of a nucleophilic attack (OH^- and $C_3F_7COO^-$ as nucleophiles) on the carbon atom of a methyl derivative of rhodium and the migration insertion of CO into the Rh–CH_3 bond. This seems unlikely because the rate constant of CO insertion into the Rh–CH_3 bond is very high (0.13 s^{-1} at 35°C) [39]. Moreover, the concentration of OH^- and the nucleophilicity of $C_3F_7COO^-$ are very low. Lin *et al.* [38] did not consider the mechanism of formation of a methyl derivative of rhodium.

We consider two conceivable mechanisms of the process under study: mechanisms with the participation of oxo complexes and coordinatively unsaturated complexes. The possibility of the intermediate formation of oxo complexes was supported by the detection of $C^{16}O^{18}O$ with the use of $^{18}O_2$; this fact can be explained by the reactions

$$L_nRh(C^{16}O)(^{18}O{=}^{18}O) \longrightarrow L_nRh{=}^{18}O + C^{16}O^{18}O, \qquad \text{(XI)}$$

$$L_nRh{=}^{18}O + CO \longrightarrow L_nRh + C^{16}O^{18}O. \qquad \text{(XII)}$$

Other paths of the formation of oxo complexes can be represented by the reactions of the hydride complexes of rhodium with molecular oxygen [40] (reaction (XIII)) and by the action of hydrogen peroxide (reaction (XIV)).

$$[Rh(CO)_2Cl_2]^- \xrightleftharpoons{HCl} [HRh(CO)_2Cl_3]^- \xrightarrow{O_2} [HOO–Rh(CO)_2Cl_3]^- \xrightarrow{H^+} [O{=}Rh(CO)_2Cl_3] + H_2O, \qquad \text{(XIII)}$$

$$[Rh(CO)_2Cl_3L] + H_2O_2 \xrightarrow[-L]{} [O{=}Rh(CO)_2Cl_3] + H_2O. \qquad \text{(XIV)}$$

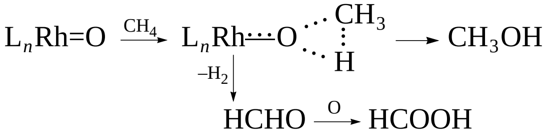
Table 2. Oxidation of titanium metal in the rhodium–copper–chloride system depending on water concentration in trifluoroacetic acid*

Entry	m_{H_2O}	*t*, min	ΔTi, wt %	O_2^{**}, vol %
1	0.50	180	4.6	0.4
2	0.62	90	3.5	0.6
3	0.70	75	7.0	0.4
4	0.80	180	7.5	0.5

* Conditions: $[RhCl_3] = 5 \times 10^{-3}$ M; Cu(II) = 0.1 g-ion/l; [NaCl] = 0.015 M. Initial pressures at T_{room}: CH_4, 6.00 MPa; CO, 1.84 MPa; O_2, 0.56 MPa. *T* = 95°C.

** O_2 denotes the residual concentration of oxygen.

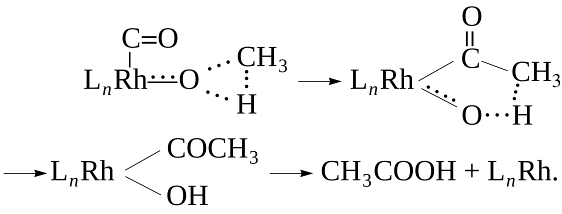
By now, it has been found using a number of examples that the oxygen atom bound to a high-valence metal atom has the property of inserting into the C–H bond of alkanes via the intermediate formation of complexes with a pentacoordinated carbon atom (these reactions were considered in [1, 2]). As a result, methanol is formed from methane (reaction (XVa)). It is likely that the biological oxidation of methane to methanol involves an analogous reaction with the participation of a binuclear complex of iron(IV). According to Shilov [2], oxo complexes can also remove a hydrogen molecule from methane to form formaldehyde. The rapid oxidation of the latter gives formic acid (reaction (XVb)).



(XVa)

(XVb)

In accordance with the hypothesis on the existence of complexes with pentacoordinated carbon, the following mechanism of acetic acid formation may be suggested:

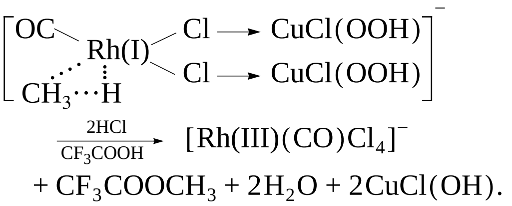


(XVI)

According to kinetic data, the formation of methyl trifluoroacetate is much more sensitive to the oxygen content of the gas phase than the formation of acetic and formic acids (Figs. 4, 5). Therefore, the course of the process can be tentatively separated into two stages. At the first stage (~45 min), the major portion of oxygen is consumed, and almost 90% methyl trifluoroacetate is formed. The concentration of intermediately formed hydrogen peroxide is low, and it further decreases at the second stage. This is supported by the fact that, with the use of the Rh(III)–Pd(II)–Cu(II) and Rh(III)–Pt(II)–Cu(II) systems, palladium and platinum metals were precipitated even at a sufficiently high O_2 content and a short reaction time. It is likely that the concentration of hydrogen peroxide is low, so that it is incapable of oxidizing palladium and platinum, which are formed under the action of CO. Because of this, at the second stage of the process, an alternative mechanism is possible, namely, the mechanism with the participation of coordinatively unsaturated Rh(I) complexes. These complexes can be formed in inner-sphere redox reactions (reactions (X) and (XVII)) [33].

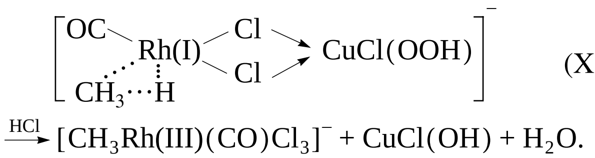
$$[Rh(CO)_2(OH)Cl_3]^- \longrightarrow [Rh(CO)Cl_2]^- + CO_2 + HCl. \qquad (XVII)$$

We found that the rhodium–copper–halide system does not catalyze the H–D isotope exchange of methane with water. Thus, in the system containing 0.01 M $RhCl_3$, 0.03 M NaCl, and 0.2 M CuO in an aqueous CF_3COO solution (m_{D_2O} = 0.62) at P_{CH_4} = 6 MPa, P_{O_2} = 0.2 MPa, and P_{CO} = 0.5 MPa, the mass spectra after 25 h of reaction revealed no isotope-exchange products of methane over the background level. Moreover, the use of the $[Rh(CO)_2Cl_2]_2$ complex in the absence of O_2 and CO (P_{CH_4} = 6 MPa) at 95°C for 15 h did not result in the formation of deuterium–hydrogen exchange products of methane with the medium either. It is most likely that the formation of a methyl carbonyl complex of rhodium (an intermediate for the production of acetic and formic acids) takes place under the action of an oxidizing agent. It is believed that methane initially forms a weak associate with a coordinatively unsaturated complex. Then, two electrons are transferred from Rh(I) via a chloride bridge and a copper atom to the hydroperoxide group bound to copper. Next, the following transformations may be considered: The transfer of two electrons from the C–H bond would result in the release of a carbocation and a proton; however, according to Shilov and Shul'pin [1], such a synchronous process is improbable. It is most likely that the heterolytic dissociation of the C–H bond occurs under the action of a base, such as CF_3COO^-. In this case, methyl trifluoroacetate and Rh(III) hydride are formed; the latter is immediately oxidized with the release of a proton by the transfer of two electrons to the second hydroperoxide group. The overall process can be represented by the reaction



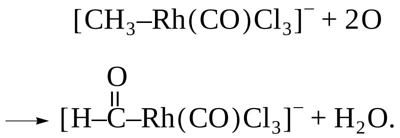
(XVIII)

In the other mechanism, two-electron transfer suffices to form the Rh(III)–methyl bond and to release a proton, which is bound as water:



(XIX)

If the methyl carbonyl complex has a chance to coordinate the second CO molecule, the subsequent transformation occurs analogously to the well-known Monsanto process [41]: the insertion of a carbonyl group into the Rh–CH_3 bond with the formation of an acyl complex. Next, acetic acid is produced by reductive elimination and hydrolysis. The double consecutive action of an oxidizing agent on the methyl monocarbonyl complex leads to a formyl derivative of rhodium and then to formic acid:



$$[CH_3{-}Rh(CO)Cl_3]^- + 2O \longrightarrow [H{-}\overset{\overset{O}{\|}}{C}{-}Rh(CO)Cl_3]^- + H_2O. \tag{XX}$$

Thus, the likelihood of the mechanism of the test process with the participation of oxo complexes is based on the formation of $C^{16}O^{18}O$ with the use of $^{18}O_2$. The possibility that coordinatively unsaturated rhodium complexes can exist was supported by the fact that in the reactions of their formation the major portion of oxygen atoms enters the resulting carbon dioxide from water and trifluoroacetic acid molecules (reactions (X) and (XVII)). The yields of products of the oxidation and oxidative carbonylation of methane as extremal functions of the concentration of chloride ions and the pressure of carbon monoxide are also consistent with the possible participation of coordinatively unsaturated rhodium(I) complexes in the activation of methane.

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