

Functionalisation of methane under dioxygen and carbon monoxide catalyzed by rhodium complexes Oxidation and oxidative carbonylation

Evgeniy G. Chepaikin^{a,*}, Anna P. Bezruchenko^a, Alla A. Leshcheva^a,
Grigoriy N. Boyko^a, Ivan V. Kuzmenkov^a,
Eduard H. Grigoryan^a, Aleksander E. Shilov^b

^a Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

^b Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

Received 19 September 2000; accepted 9 January 2001

Abstract

This work is aimed at the development of catalytic metal complex systems for the functionalisation of methane.

Methane, dioxygen, and carbon monoxide react in the presence of $\text{RhCl}_3\text{-NaCl-KI}$ system as a catalyst to form methanol, formic and acetic acids. The system activity changes on varying reaction media and increases at turning from water to aqueous organic acids, trifluoroacetic acid being the most efficient. The yield of reaction products strongly depends on mole fraction of water in the solution, carbon monoxide pressure and concentration of iodine ions. With the increase of chloride ions concentration, the yield of acetic acid passes through the maximum, the yields of methanol, formic acid and methyl trifluoroacetate decrease. The substitution of $\text{CF}_3\text{COOH-H}_2\text{O}$ for $\text{CF}_3\text{COOD-D}_2\text{O}$ results in a kinetic isotope effect in $k_{\text{H}}/k_{\text{D}} \sim 1.7\text{--}2.0$ for all the products formed. Hypoiodic acid and (or) hydrogen peroxide seem to be intermediate oxidants in the course of the reaction. Possible reaction mechanisms are considered. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxidation; Dioxygen; Carbonylation; Rhodium complexes

1. Introduction

One of the most important problems of modern chemistry is activation of alkanes, particularly, methane to involve them in selective catalytic reactions [1–13].

Thermodynamically preferable processes of methane functionalisation are oxidation and oxidative

carbonylation. These reactions could be expected to be realized selectively in the presence of homogeneous metal complex catalysts.

Lin and Sen [14] using the $\text{RhCl}_3\text{-NaCl-KI}$ system and Fujiwara and co-workers [15] using Pd compounds in CF_3COOH were the first to show the possibility of catalytic oxidative carbonylation of methane to form acetic acid under molecular oxygen and carbon monoxide.

A catalytic system including $\text{RhCl}_3\text{-NaCl-KI}$ was found to be the most promising. For example, the use of the perfluorobutyric acid–water mixture at the 6:1 volume ratio provided an essentially higher yield

* Corresponding author. Tel.: +7-095-962-80-06;

fax: +7-095-962-80-40.

E-mail addresses: echep@ism.ac.ru (E.G. Chepaikin), grig@ism.ac.ru (G.N. Boyko).

of methanol and methyl perfluorobutyrate as reaction products of oxidation of methane than in pure water [16]. Recently we have reported that the yield of acetic acid increases 5–6 times in oxidative carbonylation of methane in the $\text{RhCl}_3\text{-DCl-KI}$ system in the presence of dioxygen if water is substituted for the $\text{CD}_3\text{COOD-D}_2\text{O}$ mixture (4:1, v/v) [17,18]. In this reaction acetic acid is formed with the rate up to $0.4 \text{ mole (mole Rh)}^{-1} \text{ h}^{-1}$ that is comparable with the data reported in [16] and is the main product of methane conversion.

The mechanism of the $\text{RhCl}_3\text{-DCl (NaCl)-KI}$ catalytic system action in oxidative carbonylation of methane has not yet been definitely established. The formation of CH_3I and its oxidative addition to Rh(I) observed in carbonylation of methanol according to the method developed by Monsanto [19] can be rejected since CH_3OD or CH_3I added in the reaction mixture form methyl acetate or methyl chloride, respectively, but not acetic acid [17,18].

The data obtained witness an essential effect of a solvent nature on the yield of products in the presence of the rhodium-chloride-iodide system. Therefore, it seems to be useful to extend a number of solvents to search for the most efficient systems. One of solvents the most commonly used in functionalisation of the C–H bond both in homogeneous catalysis [2,13,15,20] and preparative organic chemistry [21] is trifluoroacetic acid. This paper reports some features of kinetics and the mechanism of oxidation and oxidative carbonylation of methane in the presence of dioxygen in the $\text{RhCl}_3\text{-NaCl-KI}$ catalytic system in aqueous trifluoroacetic acid.

2. Experimental

Special purity grade $\text{RhCl}_3\cdot(\text{H}_2\text{O})_n$ (34.5 wt.% of Rh), NaCl and KI, CF_3COOH (“chemically pure”), CF_3COOD (99.9% of D), D_2O (99.9% of D), CH_4 (99.8%), CO (99.9%) and O_2 (99.9%) were used.

Catalytic experiments were performed in a stainless steel reactor (34 cm^3) lined with a fluoroplastic. A liquid–metal contact was fully excluded and a contact of a vapor–gas phase with a metal was minimum and only in a non-heated part of the reactor. To maintain a precise water/trifluoroacetic acid ratio, the catalytic system was prepared in a special container by weigh-

ing all the ingredients including liquid ones. The total volume of the liquid phase fed to the reactor was 2.5 cm^3 . A metallic disk covered by a fluoroplastic was sunk in the reactor which was then pressurized and connected to a gas mixing setup equipped with a master manometer gage (10 MPa). The reactor was usually fed with CH_4 (6 MPa), O_2 (0.56 MPa), and CO (1.84 MPa). The reactor jacket was connected to a water thermostat pre-heated up to the experimental temperature and a shaker was switched on. The reactor was shaken in a plane arranged at an angle of 45° , the liquid flow and the disk provided intense stirring both liquid and gas phase and their contacting. After a while the reactor was quickly cooled down to 12°C , the gas phase was collected and the liquid phase was as a rule quantitatively frozen to be purified from the catalytic components. An amount of 220 mg of titanium beads of the $315\text{--}400 \mu\text{m}$ in size were used in the experiments on metallic Ti dissolution.

The analysis of the gas phase was performed with a chromatograph equipped with the 3 m long columns filled with molecular sieves (5 \AA) (O_2 , N_2 , CH_4 , CO) and 2 m long ones filled with Porapak Q (CO_2). A thermal-conductivity detector and helium as a carrier gas were used. The analytical accuracy was $\sim 10\%$. Qualitative and quantitative analyses of the liquid phase were carried out by the ^1H NMR method using a TESLA BC587A (80 MHz) spectrometer. A capillary filled with 0.171 M DMSO in CCl_4 was used as an external standard in the quantitative analysis. The samples containing $\text{CF}_3\text{COOH-H}_2\text{O}$ were analyzed by adding a weighted quantity of D_2O for lock to a weighted quantity of the reaction mixture ($\sim 1.5 \text{ g}$). The calibration curve was linear, the accuracy was 10%.

In some experiments with a nondeuterated medium liquid phase was analyzed by gas–liquid chromatography using a chromatograph equipped with a thermal-conductivity detector. The chromatographic column filled with Porapak Q and helium as a carrier gas were used. Propionic acid was used as an internal standard. The analytical accuracy worsened (from 10 to 20%) with the dosage increase from 3 to $8 \mu\text{l}$ due to the overlapping of peaks of propionic and trifluoroacetic acids at $>5 \mu\text{l}$ dosage. The dosage increase was necessary because of low concentrations of the substances to be analyzed.

Purity of initial gases and an isotopic composition of methane used in its H–D exchange reactions with a medium were analyzed by mass spectrometry.

3. Results and discussion

The studies of oxidative carbonylation of methane in the presence of the rhodium-chloride-iodide system in aqueous acetic acid showed that a strong acid, for example, HCl is a necessary catalytic component [17,18]. Since trifluoroacetic acid is sufficiently strong, there was no need to add HCl, and NaCl was added to have chloride anions. The products of methane, carbon monoxide and dioxygen interaction in the presence of the catalytic system under study were identical both in aqueous CF_3COOH and aqueous acetic acid, i.e. acetic and formic acids, methanol and methyl ester of corresponding acid, and carbon dioxide. However, the distribution of the products differs essentially and depends on the $\text{H}_2\text{O}/\text{CF}_3\text{COOH}$ ratio. Accurate studies of the effect of this parameter expressed as a mole fraction of H_2O (m) on the reaction pathway revealed the existence of maximum of the products yields, the position of this maximum for CH_3COOH at $m = 0.64$ and that for formic acid and the sum of methanol and methyl trifluoroacetate at $m = 0.61$ (Fig. 1). It was found in [16] and in the present work that CO_2 is formed only as the result of CO oxidation. The yield of CO_2 (Fig. 1) increases with m attaining a broad maximum, the ascending branch being close those of the corresponding maxima for organic products. It should be noted that in maximum points the average rates of the formation of acetic acid, formic acid and the sum of methanol and methyl trifluoroacetate are (in mole (mole Rh) $^{-1}$ h $^{-1}$): 6, 9 and 12, respectively. These values are noticeably higher than those obtained for the perfluorobutyric acid–water mixture [16]. On substituting $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ for $\text{CF}_3\text{COOD}-\text{D}_2\text{O}$, the bell-shape dependence of the product yields on m holds out, however, the position of the maxima is somewhat shifted (Fig. 2). The maximum yield of acetic acid is observed at $m \approx 0.67$, the total yield of methanol and methyl trifluoroacetate and the yield of formic acid reach maxima at $m \approx 0.63$. The yields of the reaction products decrease ~ 1.5 times in the maximum points as compared to those in a non-deuterated

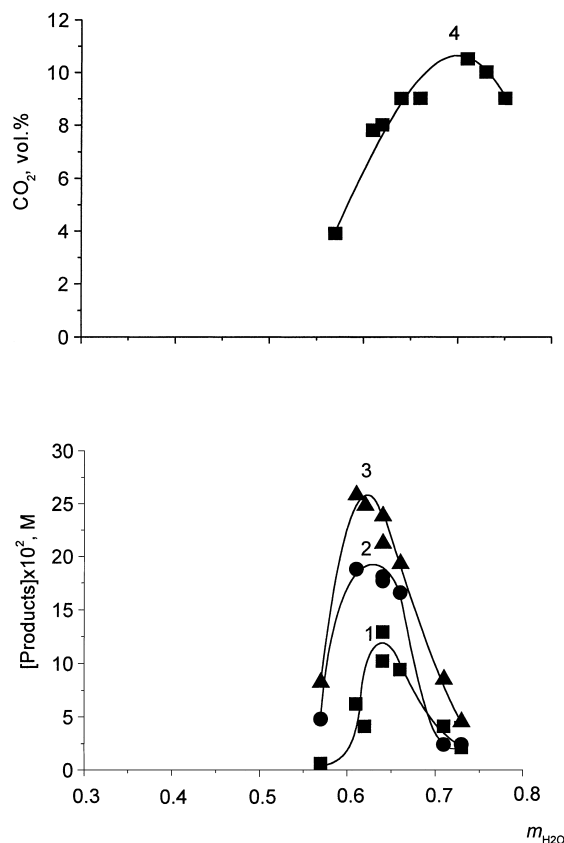


Fig. 1. Plots of organic products over period 4 h (1–3), carbon dioxide over period 2 h (4) vs. the water mole fraction in the $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ system: (1) HCOOH; (2) CH_3COOH ; (3) $\text{CF}_3\text{COOCH}_3 + \text{CH}_3\text{OH}$; (4) CO_2 . Reaction conditions: $[\text{RhCl}_3 \cdot 4\text{H}_2\text{O}] = 5 \times 10^{-3} \text{ M}$, $[\text{NaCl}] = 5 \times 10^{-2} \text{ M}$, $[\text{KI}] = 2 \times 10^{-2} \text{ M}$; $P_{\text{CH}_4}^0 = 6.00 \text{ MPa}$, $P_{\text{CO}}^0 = 1.84 \text{ MPa}$, $P_{\text{O}_2}^0 = 0.58 \text{ MPa}$; $T = 95^\circ\text{C}$. The gas phase is replaced by a fresh one every 2 h.

solvent. In a deuterated solvent the yield of CO_2 reaches the maximum with the increase of m as well (Fig. 2). Since the analytical procedure involved the ^1H NMR method, further studies were performed in $\text{CF}_3\text{COOD}-\text{D}_2\text{O}$ except for the data shown in Fig. 4.

Special experiments were carried out to clarify HCOOD stability during the reaction. An amount of 0.173 M of HCOOD was added to a starting catalytic solution (experimental conditions are shown in Fig. 3). The oxygen-free experiment was carried out for 4 h at $P = 1.84 \text{ MPa}$ at 95°C . The HCOOD quantity remained unchanged after the reaction. The

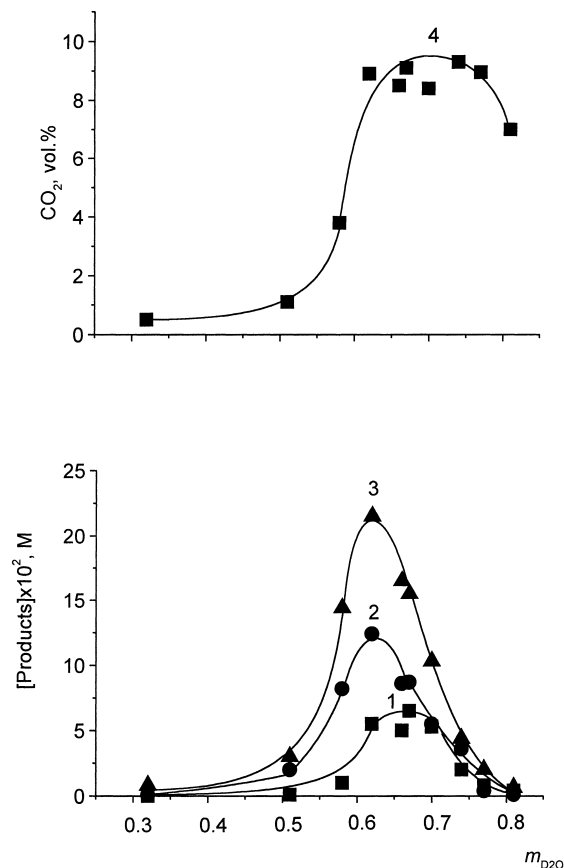


Fig. 2. Plots of organic products over period 4 h (1–3), carbon dioxide over period 2 h (4) vs. the water mole fraction in the $\text{CF}_3\text{COOD}-\text{D}_2\text{O}$ system: (1) HCOOD; (2) CH_3COOD ; (3) $\text{CF}_3\text{COOCH}_3 + \text{CH}_3\text{OD}$; (4) CO_2 . Reaction conditions: $[\text{RhCl}_3 \cdot 4\text{H}_2\text{O}] = 5 \times 10^{-3} \text{ M}$, $[\text{NaCl}] = 5 \times 10^{-2} \text{ M}$, $[\text{KI}] = 2 \times 10^{-2} \text{ M}$; $P_{\text{CH}_4}^0 = 6.00 \text{ MPa}$, $P_{\text{CO}}^0 = 1.84 \text{ MPa}$, $P_{\text{O}_2}^0 = 0.58 \text{ MPa}$; $T = 95^\circ\text{C}$. The gas phase is replaced by a fresh one every 2 h.

presence of oxygen ($P_{\text{O}_2} = 1 \text{ MPa}$) did not affect the experimental results. Thus, the decrease of formic acid observed by ^1H NMR spectra in a deuterated medium can be attributed neither to the exchange $\text{HCOOD} + \text{D}^+ \rightarrow \text{DCOOD} + \text{H}^+$ nor to oxidation $\text{HCOOD} + 1/2\text{O}_2 \rightarrow \text{CO}_2 + \text{HDO}$.

We found CH_3OD (0.155 M) added to the catalytic system (Figs. 2, $m = 0.67$) at $P_{\text{CO}} = 1.9 \text{ MPa}$ and $P_{\text{O}_2} = 0.9 \text{ MPa}$ to convert to HCOOD only by 17% for 4 h. Therefore, the contribution of methanol oxidation to the formation of formic acid is not important, no traces of CO_2 being found. These data are in agree-

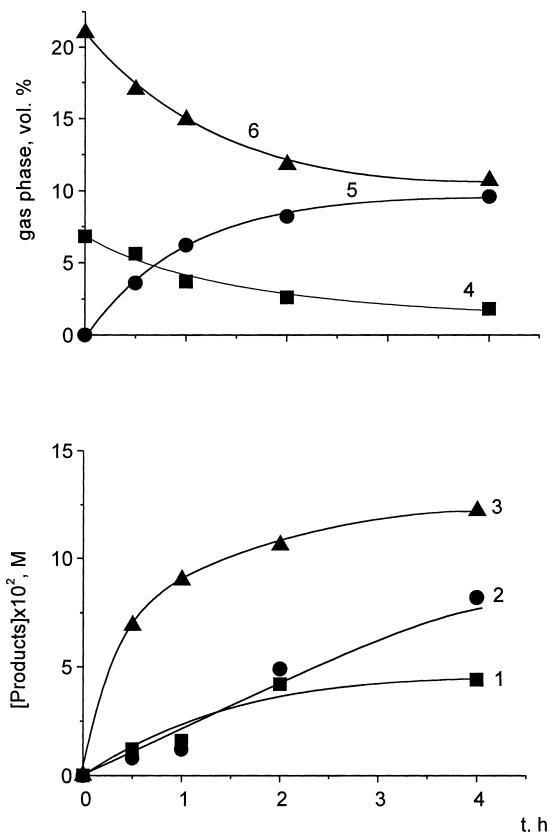


Fig. 3. Plots of organic products (1–3) and the composition of the gas phase (4–6) vs. reaction time in $\text{CF}_3\text{COOD}-\text{D}_2\text{O}$: (1) HCOOD; (2) CH_3COOD ; (3) $\text{CF}_3\text{COOCH}_3 + \text{CH}_3\text{OD}$; (4) O_2 ; (5) CO_2 ; (6) CO. Reaction conditions: $[\text{RhCl}_3 \cdot 4\text{H}_2\text{O}] = 5 \times 10^{-3} \text{ M}$, $[\text{NaCl}] = 5 \times 10^{-2} \text{ M}$, $[\text{KI}] = 2 \times 10^{-2} \text{ M}$; $m_{\text{D}_2\text{O}} = 0.67$; $P_{\text{CH}_4}^0 = 6.00 \text{ MPa}$, $P_{\text{CO}}^0 = 1.84 \text{ MPa}$, $P_{\text{O}_2}^0 = 0.58 \text{ MPa}$; $T = 95^\circ\text{C}$.

ment with those on oxidative carbonylation of methane in the rhodium-iodide-chloride system both in perfluorobutyric acid [16] and perdeuteroacetic acid [17,18] and evidences acetic acid to be formed directly from methane rather than by carbonylation of the resulting methanol.

We found that there is almost no oxidation of CO to CO_2 even at optimum m values in the absence of iodine. Special experiments showed that in contrast to the Monsanto system which uses significantly higher iodine concentrations [22], the system under study does not catalyze the water gas shift reaction (WGS) even in full absence of oxygen at $m = 0.64\text{--}0.91$ and $P_{\text{CO}} = 0.64\text{--}1.84 \text{ MPa}$ at 95°C .

The system was found not to catalyze isotope H–D exchange of methane with the medium. For example, according to mass spectra, the interaction of the system containing 0.01 M RhCl_3 , 0.04 M KI, 0.1 M NaCl, 1.8 ml of CF_3COOD , 0.7 ml of D_2O ($m = 0.63$), $P_{\text{CH}_4} = 6 \text{ MPa}$ ($\text{CH}_4:\text{Rh} = 100:1$, mole) and $P_{\text{CO}} = 1.84 \text{ MPa}$ does not yield noticeable amounts of the products of the H–D exchange of methane after 29 h at 95°C .

The analysis of kinetic curves (Fig. 3) allowed the following conclusions to be drawn. Acetic acid is accumulated almost linearly with time at least in the first 2 h. The kinetic curves for formic acid, methanol and methyl trifluoroacetate show a strong dependence of formation rates on oxygen concentration. It is seen in Fig. 3 that concentrations of dioxygen and carbon monoxide in gas phase decrease due to intense oxidation of CO. At oxygen content not less than 5–7% (volume) and $m < 0.67$ methyl trifluoroacetate is the main organic product of methane, carbon monoxide and molecular oxygen interaction in the rhodium-chloride-iodide system. However, at $m \approx 0.67$ and oxygen content less than 2–3% (volume) the rate of CH_3COOH formation is higher than those of the other products. Almost the same dependence is observed for the light solvent (Fig. 4).

The values of the initial rates of products formation and specific catalytic activity are listed in Table 1. The change from protic to deuterium containing solvent corresponds to kinetic isotope effect $k_{\text{H}}/k_{\text{D}} \sim 1.7\text{--}2.0$.

The dependence of the yield of reaction products on CO pressure shows a maximum (Fig. 5). With $[\text{Cl}^-]$ increasing up to 0.2 M, the yield of acetic acid grows and the yields of other organic products remain almost

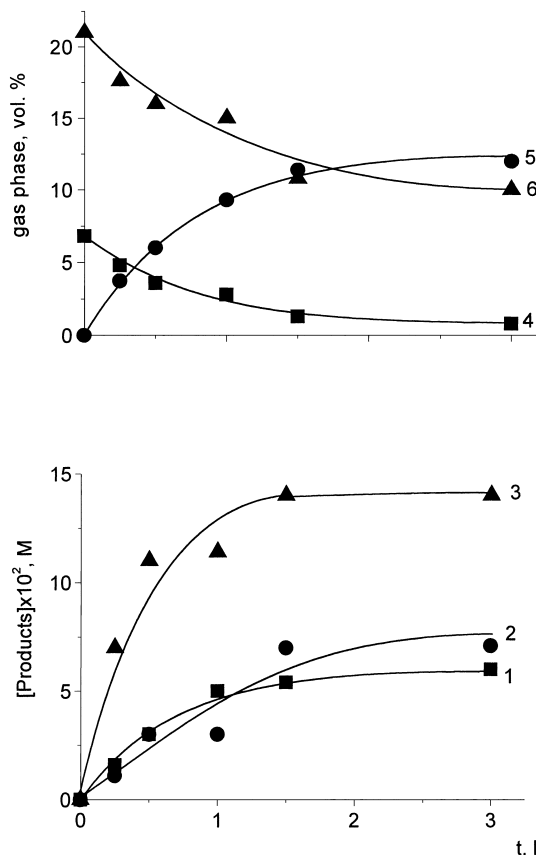


Fig. 4. Plots of organic products (1–3) and the composition of the gas phase (4–6) vs. reaction time in $\text{CF}_3\text{COOH-H}_2\text{O}$: (1) HCOOH ; (2) CH_3COOH ; (3) $\text{CF}_3\text{COOCH}_3 + \text{CH}_3\text{OH}$; (4) O_2 ; (5) CO_2 ; (6) CO . Reaction conditions: $[\text{RhCl}_3 \cdot 4\text{H}_2\text{O}] = 5 \times 10^{-3} \text{ M}$, $[\text{NaCl}] = 5 \times 10^{-2} \text{ M}$, $[\text{KI}] = 2 \times 10^{-2} \text{ M}$; $m_{\text{H}_2\text{O}} = 0.67$; $P_{\text{CH}_4}^0 = 6.00 \text{ MPa}$, $P_{\text{CO}}^0 = 1.84 \text{ MPa}$, $P_{\text{O}_2}^0 = 0.58 \text{ MPa}$; $T = 95^\circ\text{C}$.

Table 1

The values of initial reaction rates for oxidation and oxidative carbonylation of methane and oxidation of CO to CO_2 and the values of the isotope effect as to a solvent^a

Products	Solvent $\text{CF}_3\text{COOH-H}_2\text{O}$		$\text{CF}_3\text{COOD-D}_2\text{O}$		$k_{\text{H}}/k_{\text{D}}$
	$r \times 10^2$ ($\text{mole l}^{-1} \text{h}^{-1}$)	Turnover (h^{-1})	$r \times 10^2$ ($\text{mole l}^{-1} \text{h}^{-1}$)	Turnover (h^{-1})	
	Methyltrifluoroacetate and methanol	36	71	18	
Acetic acid	4.5	9.0	2.2	4.4	2.0
Formic acid	6.0	12	3.5	7.0	1.7
Carbon dioxide	650	1300	320	640	2.0

^a Conditions according to Figs. 3 and 4.

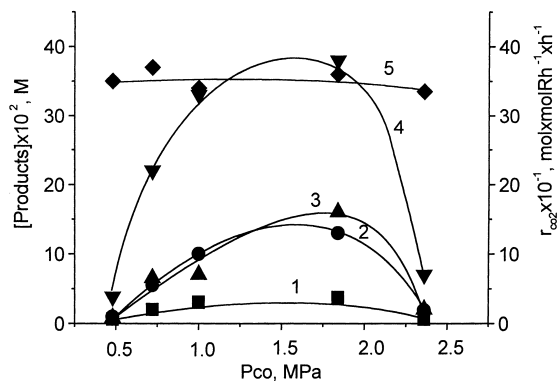


Fig. 5. Plots of organic products (1–4) and the oxidation rate CO into CO₂ (5) vs. carbon monoxide pressure in CF₃COOD–D₂O: (1) CH₃OD; (2) CH₃COOD; (3) HCOOD; (4) CF₃COOCH₃; (5) CO₂. Reaction conditions: [RhCl₃ · 4H₂O] = 5 × 10⁻³ M, [NaCl] = 5 × 10⁻² M, [KI] = 2 × 10⁻² M; m_{D₂O} = 0.67; P_{CH₄}⁰ = 6.00 MPa; P_{O₂}⁰ = 0.24 MPa; T = 95°C; t = 1 h.

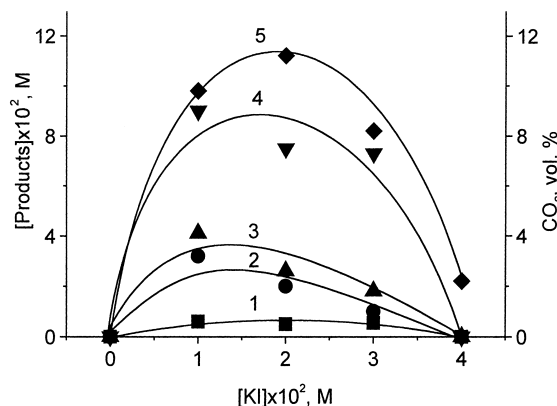


Fig. 7. Plots of organic products (1–4) and CO₂ (5) vs. KI concentration in CF₃COOD–D₂O: (1) CH₃OD; (2) CH₃COOD; (3) HCOOD; (4) CF₃COOCH₃; (5) CO₂. Reaction conditions: [RhCl₃ · 4H₂O] = 5 × 10⁻³ M, [NaCl] = 5 × 10⁻² M, m_{D₂O} = 0.67; P_{CH₄}⁰ = 6.00 MPa, P_{CO}⁰ = 1.84 MPa, P_{O₂}⁰ = 0.58 MPa; T = 95°C; t = 1 h.

unchanged. The further increase of [Cl⁻] inhibits the formation of all the products (Fig. 6). Oxidation and oxidative carbonylation of methane and oxidation of CO do not occur without I⁻. The dependence of the yield of all the products on [I⁻] passes through a maximum (Fig. 7).

The preliminary experiments on oxidative carbonylation of methane in the presence of the

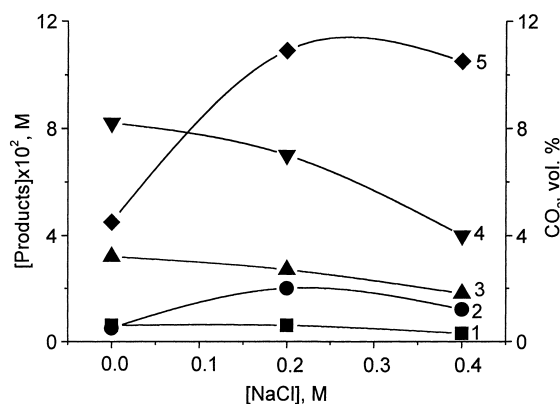


Fig. 6. Plots of organic products (1–4) and CO₂ (5) vs. NaCl concentration in CF₃COOD–D₂O: (1) CH₃OD; (2) CH₃COOD; (3) HCOOD; (4) CF₃COOCH₃; (5) CO₂. Reaction conditions: [RhCl₃ · 4H₂O] = 5 × 10⁻³ M, [KI] = 2 × 10⁻² M; m_{D₂O} = 0.67; P_{CH₄}⁰ = 6.00 MPa, P_{CO}⁰ = 1.84 MPa, P_{O₂}⁰ = 0.58 MPa; T = 95°C; t = 1 h.

rhodium–chloride–iodide system showed titanium apparatus to be unsuitable because of strong corrosion. It is known that wet iodine does not oxidize titanium [23]. We showed that titanium is absolutely resistant to the CF₃COOD–D₂O mixture at m = 0.67 and 95°C and is not oxidized in the presence of RhCl₃–NaCl or NaCl–KI under the same conditions. However, the catalytically active rhodium–chloride–iodide system produces intense oxidation of titanium in the presence of carbon monoxide and oxygen in the CF₃COOD–D₂O mixture. The maximum dissolution of metallic titanium is observed at the same m values that the maximum yield of organic products (Fig. 8). These data allow to suggest that the system components initiate oxygen and carbon monoxide to generate a sufficiently strong intermediate oxidant for both methane and titanium.

The relationships found in this work can be explained in terms of the following hypothesis. The degree of CF₃COOH dissociation increases with water content and the dependence of proton acidity on m is almost linear [24,25]. According to [26], CF₃COOD mixed with D₂O has a somewhat lower dissociation constant and a higher content of D₂O is required to attain the same acidity that in a nondeuterated solvent. This is in agreement with a small shift of the maximum yields to higher m values in a deuterated solvent (compare Figs. 1 and 2).

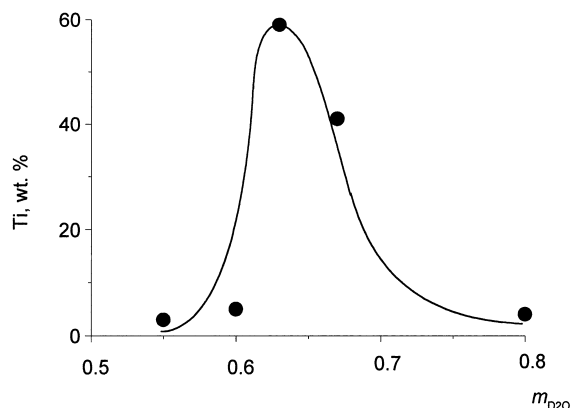


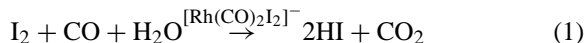
Fig. 8. Plot of titanium dissolution vs. the water mole fraction in the $CF_3COOD-D_2O$ system. Reaction conditions: $[RhCl_3 \cdot 4H_2O] = 5 \times 10^{-3} M$, $[NaCl] = 5 \times 10^{-2} M$, $[KI] = 2 \times 10^{-2} M$; $P_{CH_4}^0 = 6.00 MPa$, $P_{CO}^0 = 1.84 MPa$, $P_{O_2}^0 = 0.58 MPa$; $T = 95^\circ C$; $t = 4 h$.

Three important problems have to be discussed on considering possible mechanisms of the process:

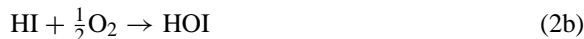
1. the nature of oxidants generated under dioxygen;
2. the formation of catalytically active Rh-containing intermediates;
3. mechanism of methane activation.

3.1. Generation of two-electron oxidants

Without a catalyst dioxygen produces free radicals in reactions with alkanes and their participation leads to non-selective processes [27]. Dioxygen reacts with reductants to generate two-electron oxidants, for example, hydrogen peroxide [1]. In the process studied such a reductant is carbon monoxide. It is seen in Figs. 1 and 2 that oxidation and oxidative carbonylation of methane are accompanied by intense catalytic oxidation of CO. Therefore, it seems important to consider the mechanism of CO oxidation in the presence of the catalytic system under study. In the absence of iodide promoter the oxidation rate decreases at least 2–3 orders of magnitude. Thus, iodine compounds function as cocatalysts. In this connection it should be noted that one of the methods for HI preparation is iodine reduction by CO in the presence of Rh complexes in aqueous acetic acid [28].



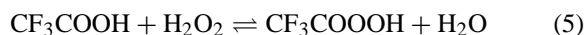
Additionally, there is a publication on HI oxidation both to I_2 and HOI [23]:



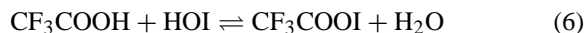
Considering the data reported in [29] we can attribute the oxidation of titanium metal (Fig. 8) to the formation of hydrogen peroxide which dissolves the surface film of TiO_2 .



It should be added that pertrifluoroacetic acid can be present in the reaction medium:

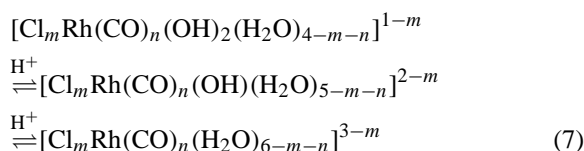


The formation of trifluoroacetyl hypoiodide (Eq. (6)) seems to be also possible but in the presence of a relatively large amount of water the equilibrium 6 must be strongly shifted to the left.

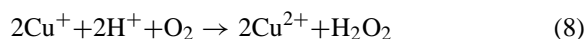


The catalytic oxidation CO to CO_2 seems to include the step of oxidative addition of I_2 to the Rh(I) carbonyl complex. The latter can be oxidized by HOI or H_2O_2 . Considering the presence of iodide and chloride ions in solution, one can suggest the occurrence of the Rh complexes as chloride, iodide and mixed compounds.

Some investigations of CO oxidation to CO_2 in the presence of catalytic systems comprising platinum-group metal compounds and cocatalysts show an bell-shape dependence on proton activity [30] and this was also observed in this work (Fig. 1). Such a maximum is explained by a protolytic equilibrium (Eq. (7)), the highest activity is manifested by an intermediate deprotonated form.



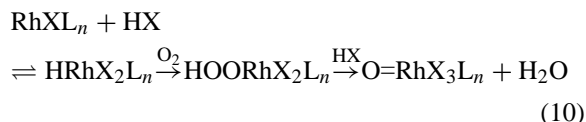
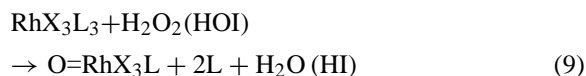
Comparing the data presented in Figs. 1, 2, and 8 one could suggest that within $m = 0.6$ – 0.7 carbon monoxide, methane and titanium are oxidized by HOI and (or) H_2O_2 . The rates of methane and titanium conversion decrease with increasing m while the rate of CO oxidation remains relatively high. It seems that the route 2b which provides the formation of two-electron oxidants is inhibited. We noted in [20] that hydrogen peroxide can be formed as a result of the Rh(I) complexes interaction with dioxygen in acidic media to form the Rh(III) hydroperoxo complex. The protonation of the latter would result in the formation of hydrogen peroxide. According to the data reported by us in [31], oxidation and oxidative carbonylation of methane are realized even in iodine-free system comprising RhCl_3 , NaCl and copper compounds. This is possible only if Cu(I) is oxidized by dioxygen to Cu(II) to form hydrogen peroxide:



The existence of reaction 8 was reported in [32]. The feature of the RhCl_3 –NaCl–Cu(I, II) system is that its activity manifests itself in a range of water concentrations essentially wider than the activity of the RhCl_3 –NaCl–KI system. This allows one to suggest that the primary intermediate of O_2 conversion to two-electron oxidants is HOI rather than H_2O_2 . The optimum interval for HOI in dependence on H_2O concentration seems to be narrower than the corresponding interval for H_2O_2 .

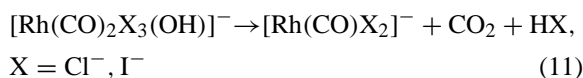
3.2. Generation of catalytically active Rh-containing species and activation of methane

We reported in [20] one of possible mechanisms when an oxo complex of high-valent rhodium can function as a catalytically active species. Such an intermediate can be formed through the following pathways:

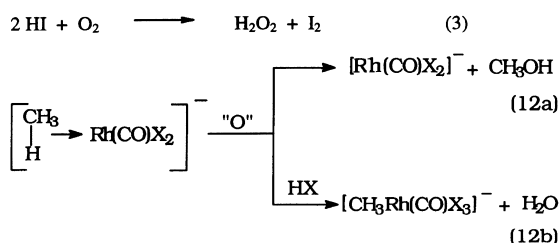


We suggest Eq. (9) to be the most probable. The intermediates of CO oxidation to CO_2 are the Rh(I) complex and possibly also Rh(III) hydride. Thus, the sequence of reaction 10 can result in the oxo complex as well [33].

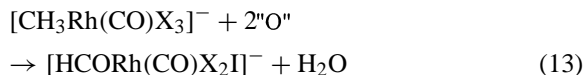
Another possible active species is a coordinatively unsaturated Rh(I) complex as a result of a redox decomposition of the Rh(III) carbonyl complex which is commonly realized in a catalytic cycle of homogeneous oxidation of CO [30].



In the first case the methane activation and further oxidation can be realized due to the formation of an intermediate complex with the five-coordinate carbon atom and O atom transfer [1,20]. In the second case, it is suggested that the principal step is an outer-sphere action of an intermediate oxidant (HOI, H_2O_2 , CF_3COOOH) (hereinafter "O") on a weak and perhaps molecular complex of methane with coordinatively unsaturated Rh(I) carbonyl halide



Such an action results in the formation of methanol (route 12a) and Rh(III) (methyl derivative (route 12b)). The second CO molecule being coordinated, the methyl complex is converted to the acyl one and then to acetic acid. A double effect of the oxidant on the methyl monocarbonyl complex results in a formic derivative and, consequently, in formic acid



However, oxygen insertion in the C–H bonds can compete with that in the Rh–CH₃ bonds in the Rh methyl derivative. In the second case, this results in the formation of the Rh methoxy complex whose protonation results in the formation of methanol.

The described mechanism can be confirmed by the data on the bell-shape dependence of the yield of reaction products on concentrations of Cl^- and I^- and CO pressure (Figs. 5–7). The rise of Cl^- and I^- concentrations and CO pressure above optimum values results in the decrease of the efficient concentration of the coordinatively unsaturated $[\text{Rh}(\text{CO})\text{X}_2]^-$ complex responsible for methane activation. The absence of the H–D exchange of methane with a medium in the presence of $[\text{Rh}(\text{CO})\text{X}_2]^-$ does not contradict to the mechanism discussed since the methyl–rhodium bond cannot be formed in the $[\text{CH}_4\text{Rh}(\text{CO})\text{X}_2]^-$ complex without an oxidant. We suggest the route with the Rh oxo complex to be realized at high content of O_2 in a gas phase and to be responsible for the main quantity of resulting methyl trifluoroacetate and methanol. This is in agreement with kinetic data (Figs. 3 and 4). The formation of acetic acid is essentially less sensitive to the content of O_2 and seems to proceed mainly through the route with the coordinatively unsaturated Rh(I) complex as an intermediate.

The H–D isotope effect in the solvent ($k_{\text{H}}/k_{\text{D}} \approx 1.7\text{--}2.0$) corresponds to the mechanism according to which the reaction rate determining step is proton transfer [34]. Obviously, the isotope effect in the reaction of CO oxidation is associated with equilibrium deprotonation of the Rh(III) aquacarbonyl complex (Eq. (7)) which can be considered a weak acid. Dissociation constants of weak acids are 2–3 times lower in D_2O than in H_2O [34]. This, in particular, is an explanation of the similar isotope effect in ethylene oxidation in the presence of Pd complexes [35], WGS on Pd phosphine complexes in aqueous trifluoroacetic acid [36] and carbonylation of acetylene in the presence of PdBr_2 in aqueous acetonitrile [37]. One of explanations of the kinetic isotopic effect for organic products can be the cleavage of the O–H bond in any possible oxidant (HOI, H_2O_2 , CF_3COOH) as a weak acid.

The role of carbon monoxide is not only the formation of acetic acid but the reduction of dioxygen. The absence of CO provides precipitation of RhI_3 and the most part of iodine is converted to molecular iodine. Thus, CO is additionally a stabilizing ligand, a reductant of I_2 in Eq. (1), and reduces Rh(III) to Rh(I) in Eq. (11). Note that reaction 11 can provide further activation of dioxygen according to the sequence 10.

A radical mechanism can also be considered. It was reported, in particular, in [38] that intense decarboxylation of trifluoroacetic acid used as a solvent is observed in methane oxidation by dioxygen in the presence of Eu compounds and Zn powder, the CF_3^\bullet radical being able to initiate methane conversion. We observed a good enough balance between CO consumed and CO_2 formed. Besides, no CF_3H was observed in the products. The accuracy of the analysis is enough to detect the presence of 0.5% of CF_3H in CO_2 . Thus, there is no reason to suggest a radical mechanism.

4. Conclusion

The work presents the results of the study of oxidation and oxidative carbonylation of methane in the presence of the $\text{RhCl}_3\text{--KI--NaCl}$ catalytic system in aqueous trifluoroacetic acid.

The yields of the reaction products pass through the maximum when a mole fraction of water is equal to 0.6–0.7. The kinetic isotope effect in the $\text{CF}_3\text{COOH--H}_2\text{O}$ and $\text{CF}_3\text{COOD--D}_2\text{O}$ solvents corresponds to the cleavage of the H–OX (D–OX) bonds in intermediate oxidants.

The reaction kinetics allows one to suggest a mechanism of methane activation by Rh oxo compounds to form intermediate complexes with a five-coordinate carbon atom at high O_2 content in a gas phase. Oxo complexes of rhodium are formed with the participation of such intermediate oxidants as H_2O_2 and HOI. Oxidation of metallic titanium also corresponds to the formation of intermediates, HOI and H_2O_2 from O_2 and CO as a reductant. At low oxygen pressure another mechanism is not excluded, i.e. methane activation by coordinatively unsaturated Rh compound to form weak associate and its further reaction with oxidants.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project # 99-03-32381a and by the US Civilian Research & Development Foundation (CRDF), award # RC2-146

References

- [1] A.E. Shilov, Metal Complexes in Biomimetic Chemical Reactions, CRC Press, Boca Raton, New York, 1997.

- [2] A. Sen, *Acc. Chem. Res.* 31 (1998) 550.
- [3] E.H. Grigoryan, *Uspekhi Khimii (Russ.)* 53 (1984) 347.
- [4] E.H. Grigoryan, *Kinet. Catal.* 40 (1999) 350.
- [5] R.D. Srivastava, P. Zhou, G.J. Stiegel, V.U.S. Rao, G. Cinquegrane, *Catalysis (London)* 9 (1992) 183.
- [6] J.L.G. Fierro, *Catal. Lett.* 22 (1993) 67.
- [7] R.H. Crabtree, *Chem. Rev.* 95 (1995) 987.
- [8] J.A. Labinger, *Fuel Process. Technol.* 42 (1995) 325.
- [9] B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, *Acc. Chem. Res.* 28 (1995) 154.
- [10] G.A. Olah, A. Molnar, *Hydrocarbon Chemistry*, Wiley, New York, 1995.
- [11] A. Sen, *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2, VCH, Weinheim, Germany, 1996, p. 1081.
- [12] S.S. Stahl, J.A. Labinger, J.E. Bercaw, *Angew. Chem., Int. Ed.* 37 (1998) 2181.
- [13] I.P. Stolyarov, M.N. Vargaftik, I.I. Moiseev, *Kinet. Catal. (Russ.)* 30 (1989) 1513.
- [14] M. Lin, A. Sen, *Nature* 368 (1994) 613.
- [15] M. Kurioka, K. Nakata, T. Jintoku, Y. Taniguchi, K. Takaki, Y. Fujiwara, *Chem. Lett.* (1995) 244.
- [16] M. Lin, T.E. Hogan, A. Sen, *J. Am. Chem. Soc.* 118 (1996) 4574.
- [17] E.G. Chepaikin, G.N. Boyko, A.P. Bezruchenko, A.A. Leshcheva, E.H. Grigoryan, *Dokl. Phys. Chem.* 353 (1997) 217.
- [18] E.G. Chepaikin, G.N. Boyko, A.P. Bezruchenko, A.A. Leshcheva, E.H. Grigoryan, *J. Mol. Catal. A.* (1998) 129.
- [19] D. Forster, *Adv. Organomet. Chem.* 17 (1979) 255.
- [20] A.P. Bezruchenko, G.N. Boyko, E.H. Grigoryan, A.A. Leshcheva, E.G. Chepaikin, A.E. Shilov, *Dokl. Phys. Chem.* 363 (1998) 396.
- [21] A.H. Haines, *Methods for the Oxidation of Organic Compounds: Alkanes, Alkenes, Alkynes, and Arenes*, Academic Press, London, 1985, p. 189.
- [22] E.C. Baker, D.E. Hendriksen, R. Eisenberg, *J. Am. Chem. Soc.* 102 (1980) 1020.
- [23] V.I. Ksenzenko, D.S. Stasinevich, *Khimiya i tekhnologiya broma, ioda i ih soedinenii (Chemistry and technology of brom, iodine and their compounds)*, Khimiya, Moscow, 1979.
- [24] G.C. Hood, O. Redlich, C.A. Reilly, *J. Chem. Phys.* 23 (1955) 2229.
- [25] A.K. Covington, J.C. Freeman, T.H. Lilley, *J. Phys. Chem.* 74 (1970) 3773.
- [26] P.K. Glasoe, F.A. Zong, *J. Phys. Chem.* 64 (1960) 188.
- [27] V.S. Arutyunov, O.V. Krylov, *Oxidative Conversion of Methane*, Nauka, Moscow, 1998, p. 162, 185.
- [28] B.P. Curtis, L.W. Fanin, F.E. Paulik, J.L. Price, *Ger. Offen Patent 2211231(1973)*, *Chem. Abstr.* 1973, 78, 138415f.
- [29] G.P. Luchinskii, *Khimiya titana (Chemistry of titanium)*, Khimiya, Moscow, 1971, p. 472.
- [30] D.V. Sokol'skii, Ya.A. Dorfman, *Kataliz ligandami v vodnykh rastvorah (Catalysis by ligands in aqueous solutions)*, Nauka, Alma-Ata, 1972, p. 336.
- [31] E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, E.H. Grigoryan, *Dokl. Phys. Chem.* 373 (2000) 105.
- [32] A. Zuberbuhler, *Helv. Chim. Acta* 50 (1967) 466.
- [33] G. Strukul, *Catalytic Oxidation with Hydrogen Peroxide*, Kluwer Academic, Dordrecht, 1992.
- [34] R.P. Bell, *The Proton in Chemistry*, Chapman and Hall, London, 1973.
- [35] I.I. Moiseev, M.N. Vargaftic, Ya.K. Syrkin, *Dokl. Acad. Nauk SSSR* 153 (1963) 140.
- [36] V.N. Zudin, V.D. Chinakov, V.M. Nikipelov, V.A. Rogov, V.B. Likhobobov, Yu.I. Yermakov, *J. Mol. Catal.* 52 (1989) 27.
- [37] L.G. Bruk, I.V. Oshanina, A.P. Kozlova, O.N. Temkin, K.Y. Odintsov, *Russ. Chem. Bull.* 47 (1998) 1071.
- [38] I. Yamanaka, M. Soma, K. Otsuka, *J. Chem. Soc. C* (1995) 2235.