ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 1, pp. 12–19. © MAIK "Nauka/Interperiodica" (Russia), 2006.
Original Russian Text © E.G. Chepaikin, A.P. Bezruchenko, G.N. Boiko, A.E. Gekhman, I.I. Moiseev, 2006, published in Kinetika i Kataliz, 2006, Vol. 47, No. 1, pp. 16–23.

HIGHLY ORGANIZED CATALYTIC SYSTEMS

# Isotope Effects in the Oxidative Functionalization of Methane in the Presence of Rhodium-Containing Homogeneous Catalytic Systems

**E. G. Chepaikin*, A. P. Bezruchenko*, G. N. Boiko*, A. E. Gekhman**, and I. I. Moiseev****

** Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

*** Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 117907 Russia*

Received October 21, 2004

**Abstract**—The combined oxidation of carbon monoxide, $CH_4$, and $CD_4$ by molecular oxygen ($^{16}O_2$ and $^{18}O_2$) in aqueous solutions of trifluoroacetic acid labeled with $^{18}O$ in the presence of rhodium and copper compounds and potassium iodide has been studied. The distribution of $^{18}O$ in isotopically substituted products suggests that oxygen entered into the methane molecule from an active oxidizing agent. This oxidizing agent was produced from molecular oxygen under the action of reagents and catalytic system components. The kinetic isotope effect observed for methane ($k_H/k_D$ = 3.9–4.3) suggests a nonradical character of the step at which the oxygen atom passes from an active oxidizing agent to the methane molecule or its fragments—transition-state components of the corresponding step.

**DOI:** 10.1134/S0023158406010034

The single-step oxidative functionalization of methane [1] belongs to the most important problems of the chemistry of $C_1$. As a rule, the gas-phase partial oxidation of methane does not provide a reasonable yield of target products because of the deep oxidation of the substrate [2]. The oxidative functionalization of alkanes with the use of metal complex catalysts [3–13] in protic media [14] is a promising alternative to the partial gas-phase oxidation of alkanes. Shilov and coworkers were the first to perform the selective oxidation of methane to methanol and methyl chloride in the $PtCl_4^{2-}$–$PtCl_6^{2-}$ catalytic system [15]. A high yield of methyl bisulfate at 90% substrate conversion was reached in the oxidation of methane in the presence of a platinum complex with 2,2'-dipyrimidine in sulfuric acid solutions [16]. The key step of these reactions—alkane activation—occurred by a mechanism similar to the electrophilic substitution mechanism (dissociative mechanism according to the terminology of Shilov) [3].

Another approach to the oxidative functionalization of alkanes consists in the activation of an oxidizing agent, that is, the conversion of an oxidizing agent into an active intermediate, whose reactivity toward an alkane is higher than that of the starting oxidation agent. This type of reactions includes various versions of uncatalyzed [17] and catalytic hydroperoxide oxidation of alkanes, starting with the Fenton system [4, p. 118]; hydrocarbon oxidation with iodosobenzene in the presence of transition metal compounds [4, p. 324]; and GIF systems [4, p. 115], including a combination of the above reaction paths of alkane oxidation.

The coupled oxidation of methane and carbon monoxide in the presence of rhodium compounds, chloride ions, and iodide ions or iron or copper salts as cocatalysts resulted in methanol and its ester [18–26]. Acetic acid (the product of the oxidative carbonylation of methane) and formic acid were detected as products in these systems. The set of the reactions that occur in these systems can be formally represented by Scheme 1.

$$CH_4 + 1/2O_2 \longrightarrow CH_3OH$$
$$CH_3OH + CF_3COOH \rightleftharpoons CF_3COOCH_3 + H_2O$$
$$CH_4 + CO + 1/2O_2 \longrightarrow CH_3COOH$$
$$CH_4 + 3/2O_2 \longrightarrow HCOOH + H_2O$$
$$CH_3OH + O_2 \longrightarrow HCOOH + H_2O$$
$$CO + 1/2O_2 \longrightarrow CO_2$$

**Scheme 1.**

It is well known that the oxidation of carbon monoxide, copper salts, and iron salts in proton-donor media can be accompanied by hydrogen peroxide formation [27–29]. Thus, in a system that includes transition metal compounds, an alkane, and oxygen, both methane activation by the direct interaction between the alkane and the complex catalyst and the activation of molecular oxygen, hydrogen peroxide, or O-centered

**Table 1.** Conditions and results of the oxidative functionalization of methane with the use of compounds labeled with the isotope $^{18}O$

| No. | Initial composition | | | Isotopic composition of TFA after experiments, arb. units (mmol) | | | Isotopic composition of the resulting methyl trifluoroacetate, arb. units (mmol) | | | Isotopic composition of carbon dioxide, %* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | oxygen | TFA, mmol | water, mmol | $CF_3CO_2H$ | $CF_3CO^{18}OH$ | $CF_3C^{18}O_2H$ | $CF_3CO_2CH_3$ | $CF_3CO^{18}OCH_3$ | $CF_3C^{18}O_2CH_3$ | $CO^{18}O$ | $C^{18}O_2$ |
| 1 | $^{18}O_2$ | $CF_3COOH$<br>23.70 | $H_2O$<br>38.8 | 100<br>(18.7) | 26.0<br>(4.8) | 2.6<br>(0.48) | 23.7<br>(0.074) | 100<br>(0.312) | 12.4<br>(0.039) | 17.2 | 1.4 |
| 2 | $^{16}O_2$ | $CF_3COOH$<br>23.70 | $H_2O$<br>7.8<br>$H_2{}^{18}O$<br>31.0 | 100 | 59.7 | 10 | 100 | 32 | 0.22 | 31.1 | 4.4 |
| 3 | $^{16}O_2$ | $CF_3COOH$<br>14.22<br>$CF_3CO^{18}OH$<br>9.48 | $H_2O$<br>39.3 | 100 | 19.7 | 3.9 | 100 | 9.2 | 0.13 | 14.3 | 1.3 |
| 4 | $^{16}O_2$ | $CF_3COOH$<br>14.22<br>$CF_3CO^{18}OH$<br>9.48 | $H_2O$<br>7.8<br>$H_2{}^{18}O$<br>31.0 | 100<br>(11.2) | 90<br>(10.1) | 21.4<br>(2.40) | 100<br>(0.29) | 44.5<br>(0.13) | 0.18<br>– | 37.1 | 6.1 |
| 5** | – | $CF_3COOH$<br>23.7 | $H_2O$<br>7.8<br>$H_2{}^{18}O$<br>31.0 | – | – | – | – | – | – | 17.2 | 1.4 |

Note: $[RhCl_3] = 2.5 \times 10^{-3}$ mol/l; $[Cu(II)] = 2.5 \times 10^{-2}$ g-ion/l; $[NaCl] = 7.5 \times 10^{-3}$ mol/l; $T = 95°C$; $P_{CH_4} = 6.0$ MPa; $P_{CO} = 1.84$ MPa; $P_{O_2} = 0.58$ MPa.

* Through a coordinatively unsaturated Rh(I) complex (Scheme 4a) or a peroxo complex (Rh=O) (Scheme 4b).

** In the gas phase, the $C^{16}O_2$ pressure is 6 atm and the helium pressure is 40 atm.

radicals can be steps of the coupled oxidation of methane and carbon monoxide.

The aim of this work was to study the main mechanism of the coupled oxidation of methane and carbon monoxide in the presence of rhodium compounds in aqueous solutions of trifluoroacetic acid containing cocatalysts and sodium chloride.

## EXPERIMENTAL

**Reagents and materials.** The following commercial reagents were used: $RhCl_3 \cdot (H_2O)_n$ (34.5 wt % Rh), NaCl, KI, CuO (chemically pure), $H_2{}^{18}O$ (80.1% $^{18}O$), $(CF_3CO)_2O$ (chemically pure), $^{18}O_2$ (atomic composition: 74.0% $^{18}O$, 13.0% $^{17}O$, and 13.0% $^{16}O$; molar composition: 59.2% $^{18}O_2$, 13.0% $^{17}O^{18}O$, 5.3% $^{17}O^{17}O$, 17.5% $^{16}O^{18}O$, 2% $^{16}O^{17}O$, and 3% $^{16}O_2$), and twice-distilled water. Trifluoroacetic acid (TFA, $CF_3COOH$) was predistilled in the presence of concentrated $H_2SO_4$; $CF_3C^{16}O^{18}OH$ (20.0% $^{18}O$) was prepared by carefully mixing freshly distilled trifluoroacetic anhydride with an equimolar amount of $H_2{}^{18}O$.

The purity of gases was as follows: $CH_4$, 99.8%; $CD_4$, 98.2%; CO, 99.9%; and $O_2$, 99.5%.

**Instruments and equipment.** Liquid and gaseous reaction products were analyzed by gas chromatography (GC) (3700 chromatograph) and $^1H$ NMR spectroscopy (Bruker AC-200 P, 200 MHz and Tesla BS 587 A, 80 MHz instruments). Gas samples were analyzed by mass spectrometry (MS) on an MI-1201 instrument. A GC–MS experiment was performed on an Automass 150 instrument (Delsi-Nermag) with a DN200 gas–liquid chromatograph (Delsi). A CPSil-5 chromatographic capillary column (25 m × 0.15 mm, $d_f = 1.2$ μm) (Chrompack) was used. Carrier gas, He; $P_{injector} = 1.2$ bar; split injector, 1 : 50; $T_{injector} = 220°C$. Column temperature program: $T_{initial} = 40°C$ (4 min); $T_{final} = 250°C$ (4 min); 10 K/min. Electron ionization, 70 eV; resolution, $2.0M$ or better (where $M = m/z$) over the range $m/z$ 18–131. For the analysis of isotopic composition, the spectra were recorded in a scan mode over an *m*/*z* range from $M = M_1 - 2$ to $M_2 + 2$, where $M_1$ is the *m*/*z* of a characteristic ion containing no isotope label and $M_2$ is the *m*/*z* of a characteristic ion containing the maximum possible amount of labeled (heavy) atoms; the scan time was 100 ms. The Lucy ver. 2.0 program package was used for the processing of GC–MS data.

For sampling, a reaction solution was placed in a gas-tight test tube with a chromatographic septum and heated to ~60°C; the headspace gas was sampled with a chromatographic syringe heated to ~50°C. A 50- to 100-μl gas sample was injected into the chromatograph.

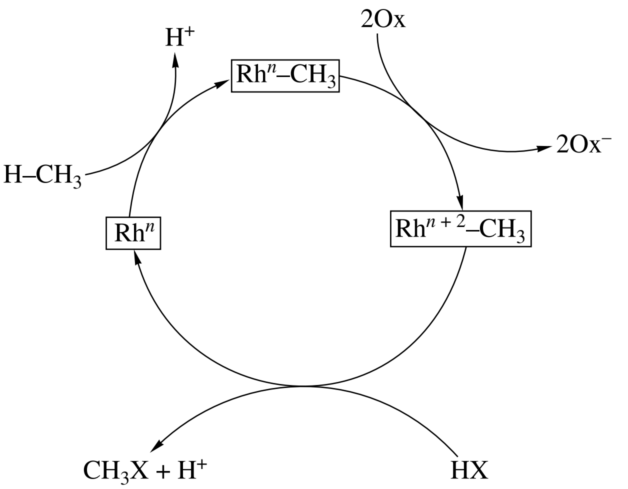
**Experiments with $^{18}$O-labeled compounds.** Experiments with the $^{18}$O-labeled molecules of $H_2O$, $CF_3COOH$, and $O_2$ were performed in accordance with a published procedure [21, 25]; the mole fraction of water was 0.61–0.62. The relative concentrations of $CF_3C^{16}O^{16}OCH_3$, $CF_3C^{16}O^{18}OCH_3$, and $CF_3C^{18}O^{18}OCH_3$ were calculated from the intensity ratios of lines with *m*/*z* 59, 61, and 63 at a maximum of the chromatographic peak of $CF_3COOCH_3$. The relative concentrations of $CF_3C^{16}O^{16}OH$, $CF_3C^{16}O^{18}OH$, and $CF_3C^{18}O^{18}OH$ were calculated from the intensity ratios of the lines with *m*/*z* 45, 47, and 49 at the maximum of the chromatographic peak of $CF_3COOH$. Table 1 summarizes the results.

**Kinetic isotope effect.** The kinetic isotope effect for methane, $k_H/k_D$, was measured in the combined oxidation of $CH_4$ and $CD_4$ in both of the systems in a $CF_3COOH$–$H_2O$ medium under the following conditions: $T = 95°C$, $P_{CH_4} = 4.0$ MPa, $P_{CO} = 1.86$ MPA, and $P_{O_2} = 0.56$ MPa. Because methane conversion in the experiments was no higher than 2%, $k_H/k_D$ was calculated from the equation $k_H/k_D = aI_{CD_4}/I_{CH_4}$, where $a$ is the ratio between the integral intensities of fragmentograms for ions with *m*/*z* 59 and 62, which correspond to $CH_3O(CO)$– and $CD_3O(CO)$– fragments, respectively; $I_{CD_4}/I_{CH_4}$ is the intensity ratio between the lines due to ions with *m*/*z* 20 and 16, which correspond to $CD_4$ and $CH_4$, respectively, in the mass spectrum of the gaseous mixture of $CD_4$ and $CH_4$ used in the experiment. Table 2 summarizes the results of these measurements.

The catalytic experiments have been described elsewhere [21, 25].

## RESULTS AND DISCUSSION

Scheme 2 illustrates a conceivable alkane oxidation mechanism [4], in accordance with which the test reaction might occur.



HX = $H_2O$, $CF_3COOH$; Ox is a one-electron oxidizing agent: $1/4\,O_2$, $1/3\,HO_2^{\bullet}$; $1/2\,H_2O_2$, $Cu^{2+}$ (Rh–Cu–Cl$^-$ system), $1/2\,I_2$, or 1/2HOI (Rh–I–Cl$^-$ system).

**Scheme 2.**

Henceforth, for the sake of simplicity, the ligand environment of rhodium and the charges of complexes are not detailed.

In aqueous TFA solutions containing $H_2{}^{18}O$, an isotopic label distribution between isotopically substituted TFA ($^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$) is rapidly established in accordance with the following equilibria:

$$CF_3C^{16}O^{16}OH + H_2{}^{18}O \rightleftharpoons CF_3C^{16}O^{18}OH + H_2{}^{16}O, \quad (I)$$

$$CF_3C^{16}O^{18}OH + H_2{}^{18}O \rightleftharpoons CF_3C^{18}O^{18}OH + H_2{}^{16}O. \quad (II)$$

The equilibrium constants of reactions (I) and (II) are close to unity, and the relation $[CF_3C^{18}O^{18}OH]/[CF_3C^{16}O^{18}OH] \approx [CF_3C^{16}O^{18}OH]/[CF_3C^{16}O^{16}OH]$ must be true for the equilibrium concentrations of isotopically substituted TFA; this relation was indeed obeyed in our experiments (Table 1, entry 1). According to Scheme 2, methyl trifluoroacetate is formed because of a nucleophilic attack of TFA or the $CF_3COO^-$ anion on the coordinated $CH_3$ group (Scheme 2, HX = $CF_3COOH$). Thus, it is to be expected that the isotopic label distribution between isotopically substituted methyl trifluoroacetates ($^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$) will be the same as in isotopically substituted TFA. However, the actual concentration of doubly labeled ($^{18}O^{18}O$) methyl trifluoroacetate was much lower than that expected from Scheme 2 (practically absent, see Table 1, entry 2). If the methylrhodium intermediate mainly reacts with more nucleophilic water, the concentration of the $^{18}O$ label in methanol will be equal to the $^{18}O$ content of labeled water in solution. However, because the esterification of aliphatic alcohols with carboxylic acids involves acyl–OH bond cleavage in the acid molecule [30], the observed amount of isotopically substituted ($^{18}O^{18}O$) methyl tri-

**Table 2.** Kinetic isotope effects for methane in the Rh–I–Cl and Rh–Cu–Cl catalytic systems in the synthesis of methyl trifluoroacetate

| Entry | Reaction time, min | $RhCl_3$–KI–NaCl* | | | $RhCl_3$–CuO–NaCl** | | |
|---|---|---|---|---|---|---|---|
| | | $CH_4/CD_4$, mol/mol | $CF_3COOCH_3/CF_3COOCD_3$, mol/mol | $k_H/k_D$ | $CH_4/CD_4$, mol/mol | $CF_3COOCH_3/CF_3COOCD_3$, mol/mol | $k_H/k_D$ |
| 1 | 30 | – | – | – | 0.732 | 2.68 | 3.84 |
| 2 | 30 | – | – | – | 1.05 | 4.35 | 4.14 |
| 3 | 90 | – | – | – | 1.05 | 4.00 | 3.81 |
| 4 | 40 | 0.62 | 2.62 | 4.36 | – | – | – |
| 5 | 120 | 0.36 | 1.62 | 4.49 | – | – | – |
| 6 | 135 | 0.88 | 3.67 | 4.17 | – | – | – |
| | | | | 4.34 ± 0.16 | | | 3.93 ± 0.18 |

Note: $T = 95°C$; initial pressures (MPa) at room temperature: $CH_4$, 4.00; CO, 1.84; $O_2$, 0.58.

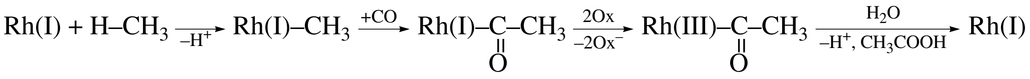
* $[RhCl_3] = 5 \times 10^{-3}$ mol/l; $[KI] = 2 \times 10^{-2}$ mol/l; $[NaCl] = 5 \times 10^{-2}$ mol/l; $m_{H_2O} = 0.67$.

** $[RhCl_3] = 2.5 \times 10^{-3}$ mol/l; $Cu(II) = 5 \times 10^{-2}$ g-ion/l; $[NaCl] = 7.5 \times 10^{-3}$ mol/l; $m_{H_2O} = 0.62$.

fluoroacetate (reaction (II)) will be considerable (approximately equal to that in the above case).

Isotopically substituted methyl trifluoroacetates ($^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$) were detected in the experiments on methane oxidation in an aqueous solution of TFA containing no $^{18}O$ labels with molecular oxygen containing 74.5 at % $^{18}O$. The relative concentration of an isotopically substituted $^{16}O^{18}O$ trifluoroacetate (73.5%) was close to the $^{18}O$ content of the initial molecular oxygen (Table 2, entry 2). Moreover, isotopically substituted ($^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$) $CO_2$ and $CF_3COOH$ were found in the reaction products (Table 1). Because $O_2$ molecules did not exchange oxygen atoms with $H_2O$ and $CF_3COOH$ in solution in the absence of CO and methane, the experimental data suggest that methane oxidation involves O atom transfer from the oxygen molecule to the substrate.

The above data allow us to exclude Scheme 2 (as a methane oxidation mechanism in the test system) from consideration. These data suggest that the activation of molecular oxygen[1] is one of the key steps in the test reaction. Nevertheless, it is likely that Rh(I) alkylation with molecular methane occurred under conditions of the test reactions. This is evident from the fact that acetic acid was also detected in the test system along with the oxidation products of methane and CO [16–25]. It is likely that acetic acid is formed by the insertion of the CO molecule into the Rh–C bond of a methylrhodium intermediate followed by the oxidation of an acylrhodium complex in accordance with Scheme 3.



$$\mathrm{Rh(I)} + \mathrm{H{-}CH_3} \xrightarrow[-\mathrm{H^+}]{} \mathrm{Rh(I){-}CH_3} \xrightarrow{+\mathrm{CO}} \mathrm{Rh(I){-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}CH_3} \xrightarrow[-2\mathrm{Ox}^-]{2\mathrm{Ox}} \mathrm{Rh(III){-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}CH_3} \xrightarrow[-\mathrm{H^+},\ \mathrm{CH_3COOH}]{\mathrm{H_2O}} \mathrm{Rh(I)}$$

Ox is a one-electron oxidizing agent.

**Scheme 3.**

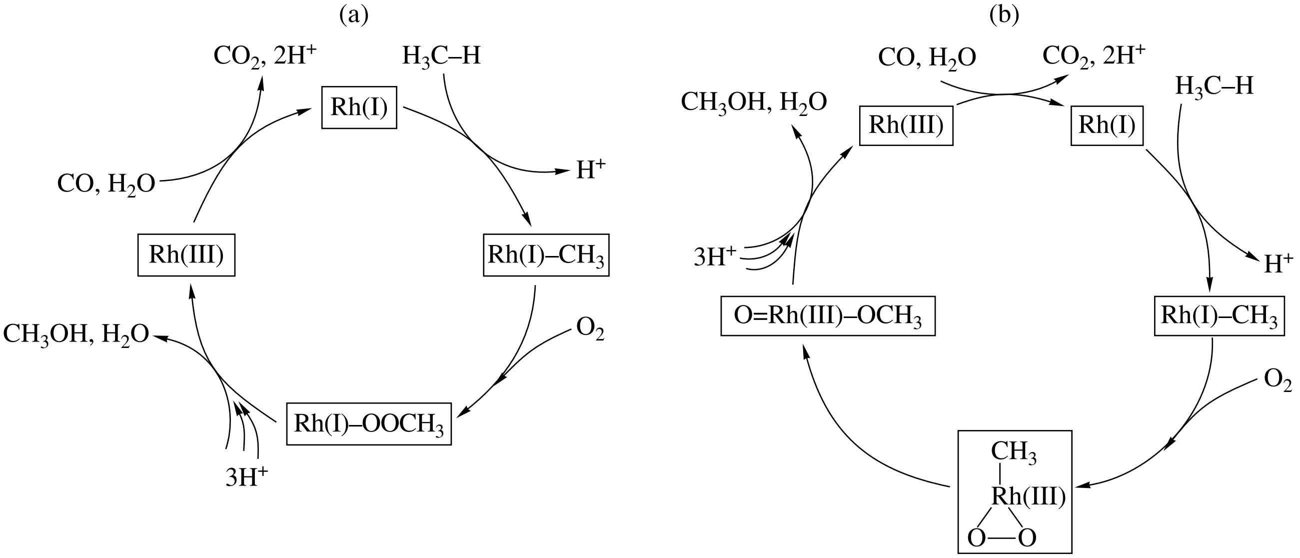
Two reaction paths (Schemes 4a, 4b) can occur with the participation of a methylrhodium intermediate, which is hypothetically formed at the first step of the combined oxidation of methane and carbon monoxide (Scheme 3).

One of these paths implies the insertion of the oxygen molecule into the metal–carbon bond (Scheme 4a) to result in an alkylperoxide complex of rhodium(I), which is converted into the detected product and a rhodium(III) complex as a result of an inner-sphere redox reaction.

According to Scheme 4b, the oxygen molecule is oxidatively added to the Rh(I) atom to form a peroxo

---

[1] The activation of molecular oxygen is considered to mean the conversion of $O_2$ into an intermediate or intermediates capable of entering into chemical reactions with the substrate or products of its interaction with the catalyst under the action of catalytic components.



**Scheme 4.**

complex.[2] The oxidation of the coordinated methyl group occurs as $CH_3$-group migration to one of the O atoms of the peroxo group (Scheme 4b).

Both of the mechanisms are consistent with the distribution of $^{18}O$ labels in methyl trifluoroacetate because a methylate fragment was formed from peroxo compounds, in which the O–O bond was retained. Therefore, the isotope exchange of O atoms with a solvent ($H_2O$ and $CF_3COOH$) did not occur (isotope exchange in η-peroxo complexes will be considered below). However, examples of molecular oxygen insertion into a metal–carbon bond (Scheme 4a) are unknown in the chemistry of platinum-group organometallic compounds. Thus, the methane oxidation mechanism involving the formation of the peroxo complexes of rhodium (Scheme 4b) seems more probable.

The step of the reduction of an oxidized catalyst species to a starting state by carbon monoxide closes both of the catalytic cycles.

The values of the catalytic isotope effect for methane in the Rh–I–$Cl^-$ and Rh–Cu–$Cl^-$ catalytic systems were practically identical and equal to 3.93 ± 0.18 and 4.34 ± 0.16, respectively (Table 2). This fact suggests that the same intermediate is responsible for methane oxidation (more exactly, C–H bond cleavage in the methane molecule) in both of the systems. The observed values of the catalytic isotope effect fall within the range 3–5 that is characteristic of hydrocarbon oxidation reactions that occur by a mechanism of hydrocarbon addition to the metal atom of a catalyst [6].

In terms of Scheme 4b, Rh(I) and Rh(III) complexes should be present in a catalytic system in the course of methane and/or CO oxidation. A binuclear Rh(II) complex can be formed by the interaction of these complexes:

$$\mathrm{Rh(I)} + \mathrm{Rh(III)} \longrightarrow \mathrm{Rh(II)}_2. \qquad \text{(III)}$$

Both trifluoroacetate groups and CO can play the role of bridging ligands to stabilize $Rh(II)_2$ dimers. These dimers are sufficiently stable to molecular oxygen [31]. Moreover, it is likely that they were not reduced to Rh(I) by carbon monoxide under the conditions of our experiments. Consequently, these complexes, which cannot catalyze the oxidation of methane or CO, are a kind of catalyst deactivation product. It is likely that the function of copper(II) chloride and iron(III) chloride cocatalysts, which are effective oxidizing agents, is reduced to the oxidation of rhodium(II) complexes. Molecular iodine ($I_2$), which is formed by the oxidation of KI with molecular oxygen in an acidic medium, is also an oxidizing agent. It is likely that all of these cocatalysts or products of their oxidation by molecular oxygen can decompose catalytically inactive rhodium(II) dimers to oxidize them to Rh(III):

$$\begin{gathered}\mathrm{Rh(II)} + 2\mathrm{Ox} \longrightarrow 2\mathrm{Rh(III)} + 2\mathrm{Ox}^-,\\ 2\mathrm{Ox}^- + 1/2\,\mathrm{O}_2 + 2\mathrm{H}^+ \longrightarrow 2\mathrm{Ox} + \mathrm{H_2O},\end{gathered} \qquad \text{(IV)}$$

where Ox = Cu(II), Fe(III), or $1/2\,I_2$.

In terms of this hypothesis, assuming that the order of a bimolecular reaction of dimer formation (reaction (III)) with respect to Rh concentration is higher than unity, the rate of reaction plotted as a function of Rh concentration would be expected to be a saturation curve. The experimentally found rate of methane oxidation as a function of the concentration $[Rh]_\Sigma$ deviated from a linear function, all other factors being the same, and it was similar in shape to the expected function (see the fig-

---

[2] The structure of this intermediate is not considered. Scheme 3 shows an η-peroxo complex by analogy with the oxygen complex $Rh(diphos)_2(O_2)Cl$.

ure); this is indirect evidence for the proposed mechanism.

Note that the participation of reoxidizing cocatalysts is a common phenomenon in metal complex catalysis. As an example, we can cite the classical homogeneous reaction of ethylene oxidation to acetaldehyde in the presence of palladium compounds. This reaction occurs in a catalytic mode only in solutions containing a cocatalyst, such as copper chloride [32]:

$$\mathrm{Pd(II)} + \mathrm{H_2C{=}CH_2} + \mathrm{H_2O} \longrightarrow \mathrm{Pd} + \mathrm{CH_3CHO} + 2\mathrm{H^+},$$

$$\mathrm{Pd} + 2\mathrm{Cu(II)} \longrightarrow \mathrm{Pd(II)} + 2\mathrm{Cu(I)},$$

$$2\mathrm{Cu(I)} + 1/2\,\mathrm{O_2} + 2\mathrm{H^+} \longrightarrow 2\mathrm{Cu(II)} + \mathrm{H_2O}.$$

In the test catalytic system, a cocatalyst (Ox) converts the catalyst from an inactive state (Rh(II)), in which it cannot react with molecular oxygen, into an active species that reacts with the substrate. Differences consist in that, in the test system, the inactive catalyst species (Rh(II)), which does not react with molecular oxygen or CO, occurs in an intermediate oxidation state (Rh(II) dimer) rather than in the lowest oxidation state as in the oxidation of alkanes by palladium(II).

For completeness, let us consider alternative mechanisms of the coupled oxidation of methane and CO. It is likely that the compounds of metals (Rh, Cu, and Fe) in low oxidation states, which are capable of reducing molecular oxygen, were present in the test catalytic system in the course of CO oxidation. The iodide ion is also a reducing agent. Therefore, the formation of $\mathrm{HO^{\bullet}}$ radicals, either free or coordinated to a metal ion, in the system cannot be excluded:

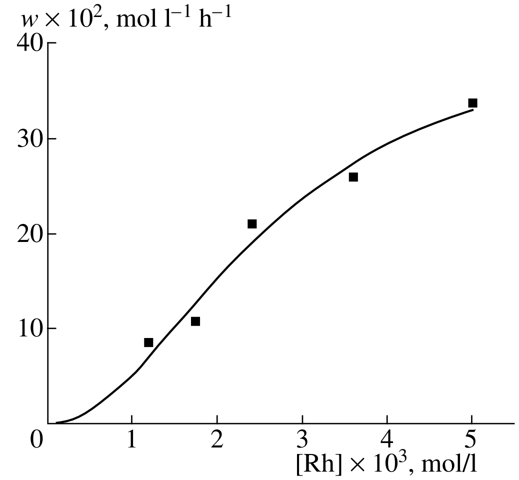
$$\mathrm{O_2} + 3\mathrm{H^+} + 3e^- \longrightarrow \mathrm{HO^{\bullet}} + \mathrm{H_2O}.$$

These radicals can abstract an H atom from methane (reaction (V)) [34] to initiate free-radical oxidation (reaction (VI)).

$$\mathrm{CH_4} + \mathrm{HO^{\bullet}} \longrightarrow \mathrm{CH_3^{\bullet}} + \mathrm{H_2O}, \qquad \mathrm{(V)}$$

$$\mathrm{CH_3^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{CH_3{-}O_2^{\bullet}}, \text{ etc.} \qquad \mathrm{(VI)}$$

This reaction scheme could explain the distribution of $^{18}$O labels in methane oxidation products. However, the addition of free-radical traps (scavengers) to reaction solutions did not affect the conversion of methane or the composition of products [21–24]. Moreover, the kinetic isotope effect of reaction (V) was 1.2–2.0 [33], whereas the kinetic isotope effect of methane oxidation reactions in the test rhodium–chloride systems was much higher (Table 2). These data allowed us to exclude from consideration the free-radical oxidation of methane in the test systems.



Dependence of the rate of formation ($w$) of methyl trifluoroacetate on the concentration of $\mathrm{RhCl_3}$. $\mathrm{CF_3COOH{-}H_2O}$; $m_{\mathrm{H_2O}} = 0.62$; $P_{\mathrm{CH_4}} = 0.60$ MPa; $P_{\mathrm{CO}} = 0.56$ MPa; $P_{\mathrm{O_2}} = 0.56$ MPa; $T = 95°\mathrm{C}$, [Rh]/[Cl$^-$] = const = 0.16; [Cu(I, II)] = 0.05 mol/l.

Data obtained in studies of the rhodium–iodide–chloride catalytic system for the oxidation and oxidative carbonylation of methane [18, 21] suggest that hydrogen peroxide was initially formed in the reaction

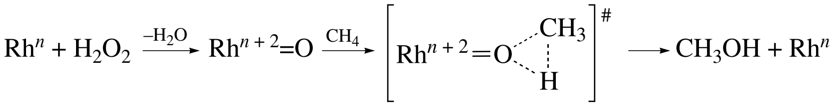
$$2\mathrm{HI} + \mathrm{O_2} \longrightarrow \mathrm{H_2O_2} + \mathrm{I_2}. \qquad \mathrm{(VII)}$$

It is also well known that, under certain conditions, copper(I) and iron(II) salts are oxidized by molecular oxygen in protic media to form hydrogen peroxide and/or the $\mathrm{HO_2^{\bullet}}$ radical [26, 27] by the reactions

$$2\mathrm{M}^n + \mathrm{O_2} + 2\mathrm{H^+} \longrightarrow 2\mathrm{M}^{n+1} + \mathrm{H_2O_2}, \qquad \mathrm{(VIII)}$$

$$\mathrm{M}^n + \mathrm{O_2} + \mathrm{H^+} \longrightarrow \mathrm{M}^{n+1} + \mathrm{HO_2^{\bullet}}. \qquad \mathrm{(IX)}$$

Melissas and Truhlar [34] described the catalytic hydroperoxide oxidation of alkanes, in particular, by hydrogen peroxide or the hydrosuperoxide radical. These reactions can occur through the oxidation of the metal atom of a catalyst by the hydroperoxide or hydrosuperoxide radical with the formation of oxene derivatives of the metal [35], which play the role of an active intermediate (Scheme 5).



$$\mathrm{Rh}^n + \mathrm{H_2O_2} \xrightarrow{-\mathrm{H_2O}} \mathrm{Rh}^{n+2}{=}\mathrm{O} \xrightarrow{\mathrm{CH_4}} \left[\mathrm{Rh}^{n+2}{=}\mathrm{O}\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\vdots}}\right]^{\#} \longrightarrow \mathrm{CH_3OH} + \mathrm{Rh}^n$$

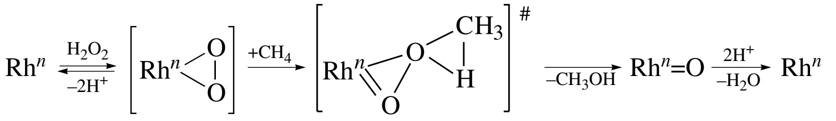
**Scheme 5.**

It is believed that the oxo complex of a metal atom in the highest oxidation state can transfer an O atom to the alkane (insert an oxygen atom into the C–H bond of the substrate). For example, Riley and Hanzlik [36] proposed this oxidation mechanism for iron(IV) and iron(V) complexes. Because Rh(III) complexes did not oxidize methane under conditions of other experiments, it is believed that Rh(IV) and Rh(V) complexes will be active in the above reaction scheme. Kinetic isotope effects for these reactions fall within the range 3–20 depending on the nature and the ligand environment of the central atom [37]. This mechanism could be supported by the values of kinetic isotope effects for the test systems (~4). However, the oxo complexes of metals in high oxidation states in aqueous media can exchange the oxygen atoms of oxo groups with the solvent:

$$M{=}O + H_2O^* \rightleftarrows M{=}O^* + H_2O. \tag{X}$$

If the reaction were to occur with the participation of an oxo complex of Rh(IV) or Rh(V), $CH_3{}^{18}OH$ would be formed in experiments performed in the presence of $H_2{}^{18}O$ because of the exchange of oxygen atoms between the oxo group of an active oxidizing agent and the solvent. As a result of the reaction with isotopically labeled $^{16}O^{18}O$ and/or $^{18}O^{18}O$ TFA, $CH_3{}^{18}OH$ would give $CF_3C^{18}O^{18}OCH_3$. The absence of methyl trifluoroacetate doubly labeled with $^{18}O$ (Table 1) casts doubts on the participation of an oxo complex of rhodium as an active oxidizing agent in methane oxidation.

The peroxo complexes[3] of rhodium can also be formed in a reaction with $H_2O_2$ or $CF_3COOH$. This complex could transfer an O atom from a peroxo ligand to a substrate molecule without changes in the oxidation state of the central atom, which plays the role of a Lewis acid, a scavenger of the remaining $O^{2-}$ atom (Scheme 6).

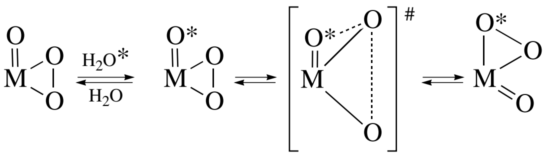


**Scheme 6.**

This can explain the efficiency of the compounds of metals in the highest oxidation states as hydroperoxide oxidation catalysts. The oxidation potential of the central atom will be insufficient for the oxidation of a coordinated peroxo group [38].

It is believed that $2 < n < 4$ in the scheme under consideration because the oxidation of a peroxo ligand would occur at $n = 4$ (especially in an acidic medium) and the Lewis acidity of Rh(II) is insufficient for the catalysis of O-atom transfer to methane. Moreover, Rh(II) is rapidly oxidized by hydrogen peroxide. The kinetic isotope effect of the catalytic hydroperoxide oxidation of alkanes to alcohols characterizes the degree of H-atom abstraction from the C atom in the transition state. Consequently, it depends on the nature of the substrate and the metal and falls within a sufficiently wide range (2.6–4.1) [39]; the values found for the test system fall within the above range.

At first glance, the distribution of $^{18}O$ in isotopically substituted products of methane oxidation is fully consistent with Scheme 6 because hydrogen peroxide is formed from molecular oxygen. Consequently, the exchange of O atoms with the solvent does not occur, and the O atom is transferred to methane from a peroxo complex, which contains the O–O band, preventing the outer-sphere isotope exchange with the solvent. However, inner-sphere isotope exchange can occur in peroxo complexes:



(XI)

This exchange was found in complexes containing a multiply bound oxygen atom; the rate of exchange depends on the nature of the central atom [40]. There is no published data on isotope exchange in the peroxo complexes of rhodium. However, this exchange is hardly to be expected for the peroxo complexes of rhodium because only aqua complexes were detected in acidic solutions of Rh(III); the exchange of an oxygen atom between a coordinated water molecule and a peroxo ligand is uncharacteristic of the aqua complexes. Thus, it is believed that the exchange of oxygen atoms of the peroxo group with oxygen atoms of a solvent in the peroxo complexes of rhodium is hindered, or it does not occur at all. Consequently, Scheme 6 seems most probable in terms of the hydroperoxide mechanism of the coupled oxidation of methane and carbon monoxide.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 02-03-33153, 05-03-32489) and through the RF President's Support to Scientific Schools Program.

---

[3] Peroxytrifluoroacetic acid, which is formed in the reaction of hydrogen peroxide with TFA, can also serve as a peroxo ligand.

## REFERENCES

1. *Kataliticheskii byulleten' nauchnogo soveta RAN po katalizu* (Bulletin of the Catalysis Council of the Russian Academy of Sciences), Novosibirsk: Inst. Kataliza, 2000.
2. Arutyunov, V.S. and Krylov, O.V., *Okislitel'nye prevrashcheniya metana* (Oxidative Conversion of Methane), Moscow: Nauka, 1998.
3. Shilov, A.E., *Aktivatsiya i kataliticheskie reaktsii alkanov* (Activation and Catalytic Reactions of Alkanes), Moscow: Mir, 1992, p. 12.
4. Shilov, A.E. and Shul'pin, G.B., *Aktivatsiya i kataliticheskie reaktsii uglevodorodov* (Activation and Catalytic Reactions of Hydrocarbons), Moscow: Nauka, 1995.
5. Shilov, A.E., *Metal Complexes in Biomimetic Chemical Reactions*, New York: CRC, 1997.
6. Rudakov, E.S., *Reaktsii alkanov s okislitelyami, metallokompleksami i radikalami v rastvorakh* (Reactions of Alkanes with Oxidizers, Metal Complexes, and Free Radicals in Solutions), Kiev: Naukova Dumka, 1985.
7. Stolyarov, I.P., Vargaftik, M.N., and Moiseev, I.I., *Kinet. Katal.*, 1989, vol. 30, no. 6, p. 1513.
8. Vargaftik, M.N., Stolarov, I.P., and Moiseev, I.I., *J. Chem. Soc., Chem. Commun.*, 1998, no. 15, p. 1049.
9. Sen, A., *Acc. Chem. Res.*, 1998, vol. 31, no. 9, p. 550.
10. Grigoryan, E.A., *Kinet. Katal.*, 1999, vol. 40, no. 3, p. 389.
11. Crabtree, R.H., *J. Chem. Soc., Dalton Trans.*, 2001, p. 2437.
12. Jia, C.G., Kitamura, T., and Fujiwara, Y., *Acc. Chem. Res.*, 2001, vol. 34, no. 8, p. 633.
13. Gol'dshleger, N.F., Tyabin, M.B., Shilov, A.E., and Shteiman, A.A., *Zh. Fiz. Khim.*, 1969, vol. 43, p. 2174.
14. Chepaikin, E.G., *Kinet. Katal.*, 2004, vol. 45, no. 3, p. 331.
15. Kushch, L.A., Lavrushko, V.V., Misharin, Yu.S., Moravsky, A.P., and Shilov, A.E., *Nouv. J. Chim.*, 1983, vol. 7, p. 729.
16. Periana, R.A., Taube, D.J., Gamble, S., *et al.*, *Science*, 1998, vol. 280, p. 560.
17. Emanuel, N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase), Moscow: Nauka, 1965.
18. Lin, M. and Sen, A., *Nature*, 1994, vol. 368, p. 613.
19. Lin, M., Hogan, T., and Sen, A., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 19, p. 4574.
20. Chepaikin, E.G., Bezruchenko, A.P., Boiko, G.N., *et al.*, *Dokl. Akad. Nauk*, 1997, vol. 353, no. 2, p. 217.
21. Chepaikin, E.G., Boyko, G.N., Bezruchenko, A.P., *et al.*, *J. Mol. Catal. A*, 1998, vol. 129, p. 15.
22. Bezruchenko, A.P., Boiko, G.N., Grigoryan, E.A., *et al.*, *Dokl. Akad. Nauk*, 1998, vol. 363, no. 3, p. 346.
23. Chepaikin, E.G., Bezruchenko, A.P., Leshcheva, A.A., *et al.*, *J. Mol. Catal. A*, 2001, vol. 169, p. 89.
24. Chepaikin, E.G., Bezruchenko, A.P., Leshcheva, A.A., and Grigoryan, E.A., *Dokl. Akad. Nauk*, 2000, vol. 373, no. 1, p. 66.
25. Chepaikin, E.G., Bezruchenko, A.P., and Leshcheva, A.A., *Kinet. Katal.*, 2002, vol. 43, no. 4, p. 550.
26. Chepaikin, E.G., Bezruchenko, A.P., Boiko, G.N., and Leshcheva, A.A., *Neftekhimiya*, 2003, vol. 43, no. 6, p. 434.
27. Zudin, V.N., Likholobov, V.A., and Ermakov, Yu.I., *Kinet. Katal.*, 1979, vol. 20, no. 6, p. 1599.
28. Zuberbuhler, A., *Helv. Chim. Acta*, 1967, vol. 50, no. 2, p. 688.
29. Huffman, R.E. and Davidson, N., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 19, p. 4836.
30. Nenitescu, C., *Chimie organič a*, Bucharest, 1960.
31. Jardine, F.H. and Sheridan, P.S., in *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed., Oxford: Pergamon, 1987, vol. 4, p. 933.
32. Moiseev, I.I., *π-Kompleksy v zhidkofaznom okislenii olefinov* (π-Complexes in Liquid-Phase Alkene Oxidation), Moscow: Nauka, 1970.
33. Gekhman, A.E., Stolyarov, I.P., Ershova, N.V., Moiseeva, N.I., and Moiseev, I.I., *Kinet. Katal.*, 2004, vol. 45, no. 1, p. 45.
34. Melissas, V.S. and Truhlar, D.G., *J. Chem. Phys.*, 1993, vol. 99, p. 3542.
35. Groves, J.T. and Watanabe, Y., *Inorg. Chem.*, 1986, vol. 25, p. 4806.
36. Riley, P. and Hanzlik, R.P., *Tetrahedron Lett.*, 1989, vol. 30, p. 3015.
37. Sorokin, A.B., Khenkin, A.M., and Shilov, A.E., *Kinet. Katal.*, 1988, vol. 29, p. 1021.
38. Tolstikov, G.A., *Reaktsii gidroperekisnogo okisleniya* (Hydroperoxidation Reactions), Moscow: Nauka, 1976.
39. Mimoun, H., *Angew. Chem., Int. Ed. Engl.*, 1982, vol. 21, p. 734.
40. Bortolini, O., Di Furia, F., and Modena, G., *J. Am. Chem. Soc.*, 1981, vol. 103, p. 3924.