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Oxidative Functionalization of Methane in the Presence of a Homogeneous Rhodium–Copper–Chloride Catalytic System: Transformation of Acetic and Propionic Acids as Solvent Components

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Abstract—The oxidative functionalization of methane (O_2, CO, 95°C, $Rh^{III}/Cu^{I,\ II}/Cl^-$ catalytic system) was studied in an aqueous acetic or propionic acid medium. It was shown that oxidative decarbonylation of carboxylic acids takes place along with methanol and methyl carboxylate formation.

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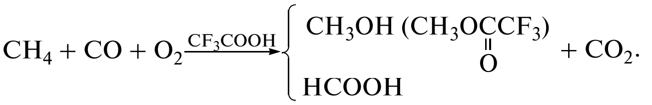
The oxidative catalytic functionalization of saturated hydrocarbons, especially methane, is one of the most important problems of petroleum chemistry and natural gas chemistry (e.g., see [1–7]). Gas-phase methane oxidation on heterogeneous catalysts does not provide satisfactory selectivity for the desired functionalized, oxygen-containing products because of their deep oxidation [8]. This is why the development of catalysts operating in the liquid phase is promising [9]. Unexpectedly, the Pd/C–$CoCl_2$ catalytic system turned out to be efficient in the functionalization of C_1–C_4 hydrocarbons by the action of O_2 and CO in trifluoroacetic acid [10], which is a reaction-stopping agent [9].

Carbon monoxide (CO) is an essential coreactant in the $Rh^{III}/I^-/Cl^-$, $Rh^{III}/Cu^{I,\ II}/Cl^-$, and $Rh^{III}/Fe^{II,\ III}/Cl^-$ – homogeneous systems for direct methane oxidation with dioxygen in aqueous trifluoroacetic acid, to give methanol (or trifluoromethyl acetate) and formic acid [11–17].



$$CH_4 + CO + O_2 \xrightarrow{CF_3COOH} \left\{\begin{array}{l} CH_3OH\ (CH_3O\overset{}{\underset{\displaystyle O}{\underset{\|}{C}}}CF_3) \\ HCOOH \end{array}\right. + CO_2.$$

Scheme 1.

The catalytic activity of these systems at 95°C and CH_4, CO, and O_2 gas pressures of 6.0, 1.84, and 0.56 MPa, respectively, attains 100–150 mol CH_4/mol Rh h). On the basis of analysis of the kinetic isotope effect (k_H/k_D) for methane and the solvent (CF_3COOD and CH_3COOD) and the results of experiments with ^{18}O-labeled H_2O, CF_3COOH, and O_2, a reaction scheme that includes the activation of methane on oxo- [11, 13, 14] and peroxo- [16] rhodium complexes has been proposed. The presence of water [7] enhances the efficiency of the $Rh^{III}/I^-/Cl^-$ and $Rh^{III}/Cu^{II}/Cl^-$ catalytic systems. To learn more about these systems, in this work we studied the behavior of propionic and acetic acids under the action of O_2 and CO in the $Rh^{III}/Cu^{I,\ II}/Cl^-$ catalytic system.

EXPERIMENTAL

Materials

The chemicals $RhCl_3 \cdot (H_2O)_n$ (Rh 34.5 wt %), NaCl, CuO, H_2SO_4, and $HClO_4$ were of the reagent grade; H_2O was doubly distilled; reagent-grade CH_3COOH was distilled; C_2H_5COOH (Merck) was used as received; *n*-heptane primary reference fuel was purified by rectification; and reagent-grade dioxane was refluxed over sodium metal over 2 h and then distilled. The gases used had the following purity: CH_4 (99.8%), CO (99.9%), O_2 (99.9%), grade A He, special purity grade nitrogen, and H_2 (99.0%). The deuterated compounds D_2O (99.9 at %), CD_3COOD (99.5 at %), and D_2SO_4 (98.0 at %) were used without further purification; CD_4 (98.2 at %) was condensed twice at a liquid nitrogen-temperature and then evaporated at –60 to –50°C for the removal of heavy impurities, e.g., CCl_4.

Catalytic experiments were carried out in a stainless steel reactor of a 34-cm^3 capacity lined with fluoroplastic. The contact of the liquid phase with the metal was completely eliminated, and the vapor–gas phase had minimal contact with the metal in the unheated part of the reactor. An $RhCl_3$ solution in H_2O or D_2O, NaCl, and CuO were loaded into the reactor, then a solvent (CH_3COOH, C_2H_5COOH, or CD_3COOD) was added. The water concentration was brought to the required value by adding an H_2SO_4/H_2O or D_2SO_4/D_2O solution. To ensure the accurate component concentrations and water/carboxylic acid ratio, the catalytic system was prepared by weighing all components, including liquid materials, in a special vessel. The total volume of the liquid phase was 2.5 or 5 cm^3. A fluoroplastic disk was placed into the reactor for better stirring, and the reactor was sealed and connected to a gas-mixing device equipped with a 10-MPa pressure gauge with a scale factor of 0.04 MPa. The reactor was fed with CH_4 (6 MPa), or a $CH_4 - CD_4$ (6 MPa) mixture, or CD_4 (4 MPa); O_2 (0.56 MPa); and CO (1.84 MPa) in the given sequence. Helium (6 MPa) was supplied instead of methane in some runs. The introduction of helium was needed in order to maintain the CO and O_2 partial pressures at a constant level for the correct comparison of the experimental results in the presence and absence of methane. In addition, this was necessary for safety reasons to prevent explosion. For the gas ratio to be varied, it is necessary first to calculate gas compositions to avoid the formation of explosive mixtures. The reactor jacket was connected to a water thermostat preliminary heated up to the experimental temperature. Experiments were carried out with intense agitation of the gas and liquid phases with the use of a shaker. When the run was over, the reactor was quickly cooled to 12°C, and the gas phase was sampled for analysis. The liquid phase was quantitatively recondensed in a vacuum into a liquid nitrogen-cooled receiver and analyzed by chromatography and H^1 NMR.

In a typical methane oxidation run, the autoclave was charged with $RhCl_3$ (6.25×10^{-3} mmol) and NaCl (18.75×10^{-3} mmol) as a solution (0.25 g) in D_2O ($[RhCl_3] = 2.5 \times 10^{-3}$ mol l^{-1} and $[NaCl] = 7.5 \times 10^{-3}$ mol l^{-1}). Then, 0.25 g of D_2SO_4 solution in D_2O ($[D_2SO_4] = 0.96 \times 10^{-3}$ mol l^{-1}), 2.27 g of CD_3COOD, and 10 mg CuO were added. The CH_4 (6.0 MPa), O_2 (0.56 MPa), and CO (1.84 MPa) gases were supplied to the autoclave. The duration of the run was 2 h.

In a typical propionic acid oxidation run, the autoclave was charged with 10 mg of CuO and 2.5 ml of the solution prepared as follows: to 1.0 ml of aqueous solution containing $[RhCl_3] = 5 \times 10^{-2}$ mol l^{-1} and $[NaCl] = 0.15$ mol l^{-1}, 1.4 ml of H_2O, 0.56 ml of H_2SO_4 in H_2O (3.9 mol l^{-1}), and 17 ml of C_2H_5COOH were added. The gases were supplied in the sequence of He (4 MPa), O_2 (0.56 MPa), CO (1.84 MPa), and He again until reaching a total pressure of 8.4 MPa. The duration of the run was 2 h.

Analysis

The gas phase was analyzed by GC (thermal conductivity detector, He) in a model 3700 chromatograph (Khromatograf experimental plant, Moscow) at 55°C. A column packed with molecular sieves 5Å (0.2–0.3 mm, 3 m × 3 mm) was used for determination of O_2, N_2, CH_4, and CO, and a 2 m × 2.5 mm Porapak Q (0.115–0.200 mm) column was used for the CO_2 analysis.

The liquid phase was analyzed by GC (flame ionization detector, N_2) on a Chrom-5 chromatograph with glass columns (2.5 mm id). Acetic acid was determined on a 2-m Separon CHN (0.115–0.200 mm) column at 130°C, with dioxane as an internal standard, and propionic acid was determined on a Separon SDA column (2.4 m) at 140°C, with *n*-heptane as an internal standard. The products of CH_4 oxidation in CD_3COOD/D_2O were analyzed by ^1H NMR on a Brucker AC-200 P spectrometer (200 MHz) and a Tesla BS 587 A spectrometer (80 MHz). The admixture of CHD_2COODin CD_3COOD was used as an internal standard in quantitative measurements.

The initial CH_4/CD_4 ratio was measured by mass spectrometry with an MI-1201 instrument equipped with a needle leak valve, a prevacuum vessel pressure of 10^{-1} torr, an electron ionization energy of 70 eV, and an ionization current of 0.2 mA. The GC/MS determination was conducted on an Automass 150 instrument (Delsi-Nermag) with a DN200 gas-liquid chromatograph (Delsi), using a CPSil chromatographic column of 5 25 m × 0.15 mm, $d_f = 1.2$ μm (Chrompack); He as the carrier gas in the constant pressure (1.2 bar) mode; split injection at a split ratio of 1 : 50 and 50. $T_{inj} = 220$°C; and the following temperature programming: $T_{in} = 40$°C (4 min), $T_{rf} = 250$°C (4 min), 10°C/min. In the electron ionization mode, resolution was at least 2.0 M (where M = *m/z*) in the range of *m/z* 18–131. To analyze the isotopic composition, the spectra were recorded in the scanning mode over the range of *m/z* 15–100, at a scanning time of 100 ms. The software suites Lucy ver.2.0 and AMDIS ver. 2.62 were used for the processing of the GC/MS results. To sample the reaction solution, it was placed in a test tube sealed with a membrane, heated up to ~60°C, and head-spaced with a chromatographic syringe heated to ~50°C. The amount of the gas phase injected into the chromatograph was 50–100 μl.

RESULTS AND DISCUSSION

It was found that the oxidation of methane does not proceed in dioxane, tetrahydrofuran, and acetonitrile in the presence of $Rh^{III}/Cu^{I,II}/Cl^-$ both in pure solvents and with addition of water or H_2SO_4.

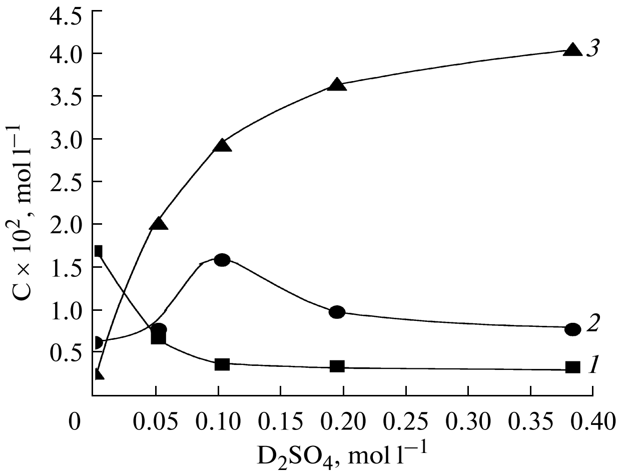


Fig. 1. The product yield in the methane oxidation as a function of D_2SO_4 concentration in CD_3COOD at the mole fraction of water $mD_2O = 0.6$: (*1*) CH_4, (*2*) CH_3OD, and (*3*) $CH_3OC(O)CD_3$; $[RhCl_3]$ 2.5×10^{-3} mol l^{-1}, $[Cu^{II}] = 5.0 \times 10^{-2}$ mol l^{-1}, $[NaCl] = 7.5 \times 10^{-3}$ mol l^{-1}, $CH_4 = 6$ MPa, $O_2 = 0.56$ MPa, CO = 1.84 MPa, $T = 95°C$, 2 h.

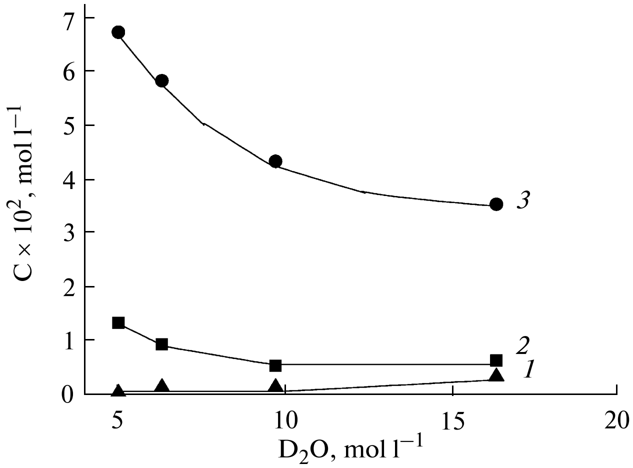
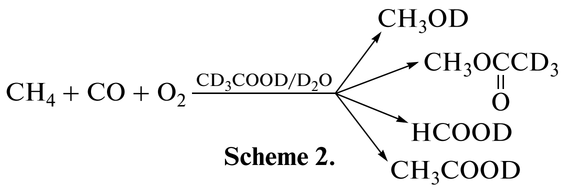


Fig. 2. The product yield in the methane oxidation as a function of D_2O concentration in CD_3COOD at $[D_2SO_4] = 0.19$ mol l^{-1}: (*1*) CH_3OD, (*2*) CH_3COOD, and (*3*) CD_3COOCH_3; $[RhCl_3]$ 2.5×10^{-3} mol l^{-1}, $[Cu^{II}] = 5.0 \times 10^{-2}$ mol l^{-1}, $[NaCl] = 7.5 \times 10^{-3}$ mol l^{-1}, $CH_4 = 6$ MPa, $O_2 = 0.56$ MPa, CO = 1.84 MPa, $T = 95°C$, 2 h.

In the CD_3COOD/D_2O medium, the CH_4 oxidation in the $Rh^{III}/Cu^{I,II}/Cl^-$ system affords the products shown in Scheme 2:



Scheme 2.

To activate dioxygen in the rhodium–copper–chloride catalytic system, a reducing agent is required. When CO is used as a reductant, acetic acid is found in the reaction products and the intensive catalytic oxidation of CO to CO_2 simultaneously occurs (reaction (1))

$$CO + 1/2O_2 \xrightarrow{Rh^{III}/Cu^{II}/Cl^-} CO_2. \qquad (1)$$

Free radicals do not contribute to methane oxidation under the conditions of our experiments [16].

Methanol is the major product in the absence of sulfuric acid[1] Unexpectedly, acetic acid without the nondeuterated methyl group was found in the products. This product may be formed if methanol gives acetic acid in the reaction with CO [18]. However, methanol and methyl iodide do not interact with CO in the presence of O_2 under our experimental conditions[2], and are converted into methyl trideuteroacetate and methyl chloride, respectively [13, 17]. Thus, the mechanism of acetic acid formation during the oxidative carbonylation of methane (Scheme 1, Fig. 1) must differ from that of the formation of acetic acid from methanol and CO catalyzed by rhodium iodide compounds (Monsanto process) [18].

The acidity of the medium has an effect on the composition and the yield of the methane oxidation products: as $[D_2SO_4]$ is increased, methyl acetate becomes the major product, the methanol yield decreases, and a small maximum in the acetic acid yield is observed (Fig. 1). If the methanol yield dropped as a result of its D_2SO_4-catalyzed esterification, the total concentration of methyl acetate and residual methanol would be constant. However, this was not the case. Consequently, methane hydroxylation or acetoxylation are significantly accelerated by the action of D_2SO_4.

At the given concentration of deuterosulfuric acid $[D_2SO_4] = 0.19$ mol l^{-1}, the decrease in the D_2O concentration to 5 mol l^{-1} slightly increases the yield of acetic acid and significantly increases the total yield of methyl acetate and methanol. However, there is no oxidation in glacial acetic acid. These two observations support the hypothesis that the reaction with methane yielding the products observed involves the nucleophilic attack of the water or acetic acid molecule. Within the range of 0–5 mol l^{-1}, there is an optimal water concentration at which the yield of methyl acetate attains the maximum.

The amount of methyl acetate formed under the experimental conditions exceeds by at least an order of magnitude the amount of the catalyst (rhodium) loaded both in the presence (table, run 5) and in the

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[1] Sulfuric acid was added to the solution in certain runs with acetic or propionic acid, in order to increase the acidity to the level corresponding to CF_3COOH.

[2] $RhCl_3 = 1.5 \times 10^{-2}$ mol l^{-1}, $KI = 2.5 \times 10^{-2}$ mol l^{-1}, $DCl = 0.12$ mol l^{-1}, $CD_3COOD–D_2O$.

Catalytic oxidative functionalization of methane in aqueous acetic and propionic acids. $[RhCl_3] = 2.5 \times 10^{-3}$ mol l^{-1}, $[NaCl] = 7.5 \times 10^{-3}$ mol l^{-1}, $[Cu^{I, II}] = 5 \times 10^{-2}$ mol l^{-1}, $T = 95°C$, $P_{O_2} = 0.56$ MPa, $P_{CO} = 1.84$ MPa, 2 h

No.	Organic acid	Water, mol l^{-1}	Inorganic acid, mol l^{-1}	Methane[a)]	Products[b)]
1	2	3	4	5	6
1	CH_3COOH	H_2O 8.0	H_2SO_4 0.2	$CH_4 : CD_4 = 0.76$	$CH_3COOCH_3 : CH_3COOCD_3 = 78$
2[c)]	CH_3COOH	H_2O 8.0	H_2SO_4 0.2	$CH_4 : CD_4 = 0.81$	$CH_3COOCH_3 : CH_3COOCD_3 = 67$
3	CD_3COOD	D_2O 17.1	0	CH_4	$CD_3COOCD_3 : CD_3COOCH_3 = 1.83$
4	CH_3COOH	H_2O 16.0	0	CD_4	$CH_3COOCH_3 : CH_3COOCD_3 = 17.5$
5	CH_3COOH	H_2O 7.7	H_2SO_4 0.2	CH_4	CH_3COOCH_3 (5.5×10^{-2} M)
6	CH_3COOH	H_2O 7.0	H_2SO_4 0.2	0[d)]	CH_3COOCH_3 (3.1×10^{-2} M)
7	C_2H_5COOH	H_2O 16.0	$HClO_4$ 0.22	$CH_4 : CD_4 = 0.14$	$C_2H_5COOCH_3$, $C_2H_5COOC_2H_5$,
8	C_2H_5COOH	H_2O 16.0	–	CD_4	$C_2H_5COOCH_3$, $C_2H_5COOC_2H_5$
9	C_2H_5COOH	H_2O 7.0	H_2SO_4 0.1	CD_4	$C_2H_5COOCH_3$, $C_2H_5COOC_2H_5$
10	C_2H_5COOH	H_2O 7.0	H_2SO_4 0.1	CH_4	$C_2H_5COOCH_3 : C_2H_5COOC_2H_5 = 1.9$
11	C_2H_5COOH	H_2O 7.0	H_2SO_4 0.11	0[d)]	$C_2H_5COOCH_3 : C_2H_5COOC_2H_5 = 1.7$

Notes: a) CH_4 (6.0 MPa), CD_4 (4.0 MPa) + He (2.0 MPa); b) the qualitative composition and the ratio were determined by GC/MS; c) reaction time, 1 h; d) methane is substituted by helium.

absence of methanol (table, run 6). Thus, methane is not the only source of methanol and its ester. At least a portion of these products is formed from acetic acid, the solvent component. This makes it impossible to measure the isotopic kinetic effect k_{CH_4}/k_{CD_4} by the method of competitive reactions; i.e., in the joint oxidation of methane and tetradeuteromethane. For example, in the oxidation of the $CH_4 : CD_4 = 0.76$ mixture, the light and heavy esters are formed in acetic acid in a ratio of ~70, which cannot be explained (table, runs 1, 2).

Note that in the CD_3COOD/D_2O system, **H**COOD, **CH_3**COOD, **CH_3**OD, and **CH_3**OC(O)CD_3 can be formed from **CH_4** only. Taking this circumstance into account, we can approximately estimate the KIE for methane in acetic acid as $((k_H/k_D) \approx 6)$ from the ratio of ~6 of the products of CH_4 and CD_4 oxidation in CD_3COOD and CH_3OOH, respectively (table, runs 3, 4).[3]

Unexpectedly, it turned out that neither the oxidation of CD_4 nor the joint oxidation of CH_4 and CD_4 in propionic acid yields deuterated products (table, runs 7–9). Nevertheless, not only methyl propionate expected as a methane oxidation product, but also ethyl propionate was formed in these runs, which, in principle, cannot result from nonradical oxidation of methane. The absence of deuterated methyl propionate[4] in the reaction products cannot be accounted for by the fact that the CD_4 oxidation rate in propionic acid (as in the case of acetic acid) is sixfold lower than the rate of CH_4 oxidation. Moreover, when methane is replaced with helium, the same products are formed and almost in the same ratios (table, runs 10, 11). All these observations indicate that methane is not subjected to oxidation in propionic acid, unlike the cases of acetic acid, and does not participate in the formation of methyl propionate. Being far from the carboxylic group, the methyl group of propionic acid probably behaves as a saturated hydrocarbon and competes with sparingly soluble methane in the reaction of the active intermediate.

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[3] It is assumed that the reaction is first-order in methane and KIE = 1 for the solvent, as in the case of $CF_3COOH(D)$ [14].

[4] The analytical procedures used in this work allowed for the determination of methyl propionate in a concentration of 10^{-3} mol/l.

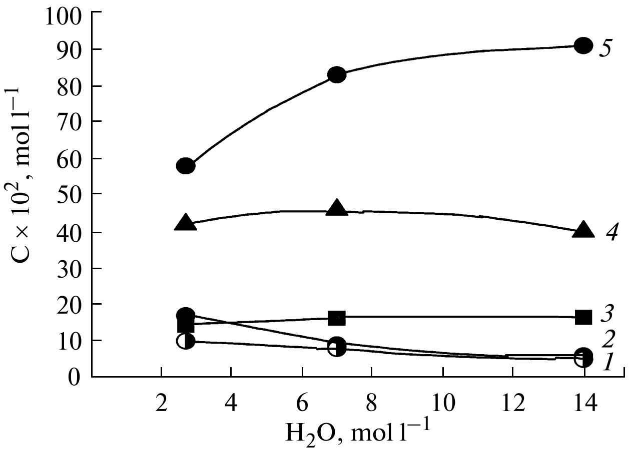


Fig. 3. The product yield in the propionic acid oxidation as a function of H_2O concentration in the absence of H_2SO_4: (*1*) $C_2H_5COOC_2H_5$, (*2*) $C_2H_5COOCH_3$, (*3*) C_2H_5OH, (*4*) CH_3COOH, and (*5*) CH_3OH; [$RhCl_3$] 2.5×10^{-3} mol l^{-1}, [Cu^{II}] = 5.0×10^{-2} mol l^{-1}, [NaCl] = 7.5×10^{-3} mol l^{-1}, He = 6 MPa, CO = 1.84 MPa, O_2 = 0.56 MPa, T = 95°C, 2 h.

Methyl propionate, ethanol, ethyl propionate, and acetic and formic acids were found in the products of propionic acid oxidation (Figs. 3–5).

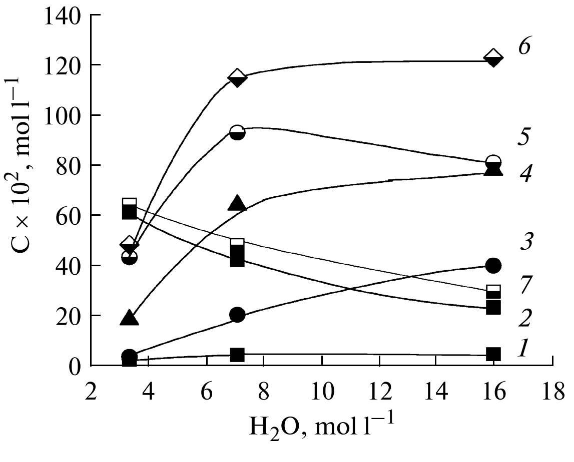


Fig. 4. The product yield in the propionic acid oxidation as a function of H_2O concentration: (*1*) C_2H_5OH, (*2*) $C_2H_5COOC_2H_5$, (*3*) CH_3OH, (*4*) CH_3COOH, (*5*) $C_2H_5COOCH_3$, (*6*) CH_3OH + $C_2H_5COOCH_3$, and (*7*) C_2H_5OH + $C_2H_5COOC_2H_5$; [$RhCl_3$] 2.5×10^{-3} mol l^{-1}, [Cu^{II}] = 5.0×10^{-2} mol l^{-1}, [NaCl] = 7.5×10^{-3} mol l^{-1}, [H_2SO_4] = 0.1 mol l^{-1}, He = 6 MPa, CO = 1.84 MPa, O_2 = 0.56 MPa, T = 95°C, 2 h.

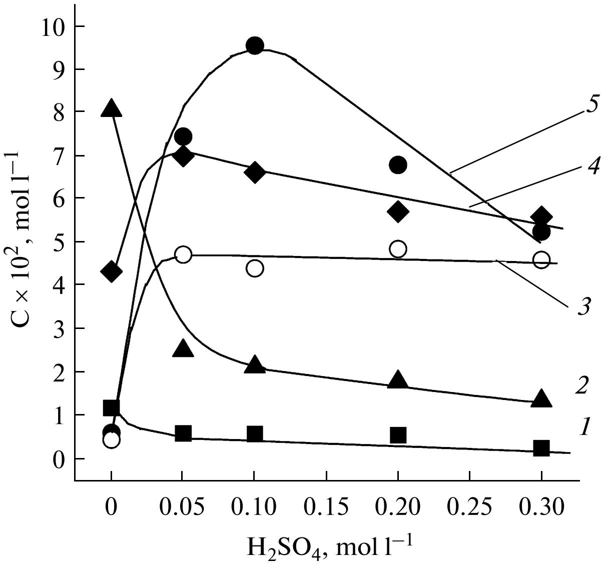


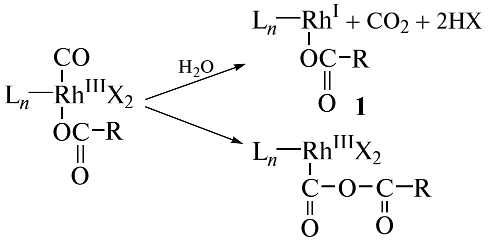
Fig. 5. The product yield in the propionic acid oxidation as a function of H_2SO_4 concentration: (*1*) C_2H_5OH, (*2*) CH_3OH, (*3*) $C_2H_5COOC_2H_5$, (*4*) CH_3COOH, and (*5*) $C_2H_5COOCH_3$; [$RhCl_3$] 2.5×10^{-3} mol l^{-1}, [Cu^{II}] = 5.0×10^{-2} mol l^{-1}, [NaCl] = 7.5×10^{-3} mol l^{-1}, [H_2O] = 7.0 mol l^{-1}, He = 6 MPa, CO = 1.84 MPa, O_2 = 0.56 MPa, T = 95°C, 2 h.

For interpretation of the mechanism of the transformation of carboxylic acids, it is important that no transformation products of acetic and propionic acids have been found in an He, He + O_2, or He + CO atmosphere. Thus, the decarbonylation of these acids requires the presence of both CO and O_2:

$$2\,RC(O)OH + CO + O_2 \longrightarrow RC(O)OR + 2CO_2 + H_2O \qquad (2)$$

$$R = CH_3, C_2H_5.$$

Although the mechanism of the reaction under study is complex, some preliminary conclusions can be made. The stability of propionic acid in the absence of CO indicate the participation of CO in decarbonylation. The stoichiometric oxidation of carbon monoxide with rhodium(III) compounds involves the intermediate formation of the rhodium(III) complex with CO [19]. Therefore, the oxidative decarbonylation of carboxylic acids and the oxidation of CO can be considered coupled reactions with the same intermediate. The rhodium(III) complex with CO and carboxylic acid can be this intermediate. Most of the amount of CO (~90%) is oxidized to CO_2 according to reaction (1) under our experimental conditions. Carbon dioxide can be formed from rhodium(III) carbonyl acetate (**1**) via two routes. One is the nucleophilic attack of water on coordinated CO and the reduction of rhodium(III) to rhodium(I) (Scheme 3, reaction (3)). The other involves the intrasphere attack of the coordinated carboxylate anion on coordinated CO and the intermediate formation of complex **2** (Scheme 3, reaction (4)). Both reactions are well known in the coordination chemistry of palladium [20].



$$L_n\text{—}\overset{CO}{Rh^{III}}X_2(OC(=O)R) \xrightarrow{H_2O} L_n\text{—}Rh^{I}(OC(=O)R) + CO_2 + 2HX \quad (3)$$

$$L_n\text{—}\overset{CO}{Rh^{III}}X_2(OC(=O)R) \longrightarrow L_n\text{—}Rh^{III}X_2(C(=O)\text{—}O\text{—}C(=O)\text{—}R) \quad (4)$$

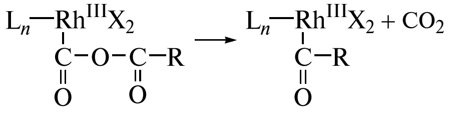
1, **2**

X = OH⁻, Cl⁻, RCOO⁻

Scheme 3.

An increase in the water content should promote reaction (3). Indeed, the yield of the decarbonylation products decreases with an increase in the water concentration (Fig. 4; curves *1*, *2*, *7*), thereby confirming indirectly the truth of the assumption on which Scheme 3 is based. It is likely that the coordinated hydroxyl ion, rather than the free water molecule, attacks the coordinated CO molecule in reaction (3), as in the case of oxidation of olefins with palladium(II) salts [21]. Indeed, the admixtures of sulfuric acid increase the yield of the decarbonylation products by decreasing the fraction of hydroxo complexes (Fig. 3; curves *1*, *3*; Fig. 4, curves *1*, *2*, *7*).

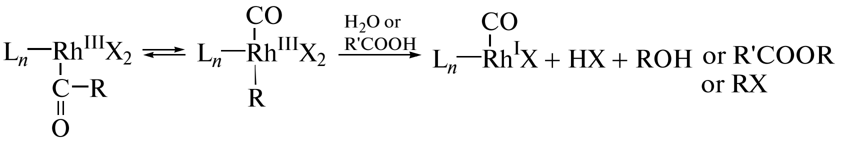
Compounds of type **2** can eliminate CO_2 to give the acyl complex of type **3** [20]. This is another CO_2 formation route:



$$L_n\text{—}Rh^{III}X_2(C(=O)\text{—}O\text{—}C(=O)\text{—}R) \longrightarrow L_n\text{—}Rh^{III}X_2(C(=O)\text{—}R) + CO_2 \quad (5)$$

2 **3**

Complex **3** is similar to the intermediate in the Monsanto process [18], the key stage of which is the reversible intrasphere insertion of CO in the Rh–C bond. We assume that complex **3** is in equilibrium with its isomer **4**, which interacts with a nucleophilic agent (water or carboxylic acid) to give the corresponding alcohol or ester:



$$L_n\text{—}Rh^{III}X_2(C(=O)\text{—}R) \rightleftharpoons L_n\text{—}\overset{CO}{\underset{R}{Rh^{III}}}X_2 \xrightarrow[R'COOH]{H_2O\text{ or}} L_n\text{—}\overset{CO}{Rh^{I}}X + HX + ROH \text{ or } R'COOR \text{ or } RX.$$

3 **4**

The suggested scheme agrees with the fact of the formation of ethanol and ethyl propionate from propionic acid or methanol and methyl acetate from acetic acid.

Within the framework of this scheme, the role of copper reduces to the reoxidation of rhodium(I) in the catalytic cycle with respect to copper (reactions (6) and (7)):

$$2Cu^{II} + Rh^{I} \longrightarrow 2Cu^{I} + Rh^{III}, \quad (6)$$

$$2Cu^{I} + ½O_2 + 2H^{+} \longrightarrow 2Cu^{II} + H_2O. \quad (7)$$

Hydrogen peroxide can appear as a result of the reactions of both Rh(I) and Cu(I):

$$Rh^{I} + O_2 + 2H^{+} \longrightarrow Rh^{III} + H_2O_2, \quad (8)$$

$$2Cu^{I} + O_2 + 2H^{+} \longrightarrow 2Cu^{II} + H_2O_2. \quad (8a)$$

The formation of hydrogen peroxide was observed during the oxidation of Cu^{I} to Cu^{II} with molecular oxygen [22].

The considered reaction sequence does not contradict the experimental results, but it does not cover all reactions occurring in the $Rh^{III}/Cu^{II}/Cl^{-}$/propionic acid system. The fact of the methanol formation in the oxidative decarbonylation of propionic acid confirms this statement. Moreover, the yields of methanol + methyl propionate and ethanol + ethyl propionate depend on the concentrations of H_2O and H_2SO_4 in different manners: the [methanol + methyl propionate] concentration increases, whereas [ethanol + ethyl propionate] decreases, with an increase in the water concentration (Figs. 3, 4); with an increase in the concentration of H_2SO_4, [methanol + methyl propionate] passes through a maximum, and [ethanol + ethyl propionate] does not change (Fig. 5). This leads to the conclusion that the formation of methanol and ethanol (and their esters) involves different active intermediates.

In the reactions of propionic acid, acetic acid, methanol, and methyl propionate are not formed in the sequence of transformations $C_2H_5COOH \longrightarrow C_2H_5OH \longrightarrow CH_3COOH$ and the subsequent decarbonylation of CH_3COOH according to the mechanism given above, because the joint oxidation of C_2D_5OD and propionic acid yields only deuteroethyl propionate ($C_2H_5COOC_2D_5$), rather than acetic acid deuterosubstituted, at the methyl group.

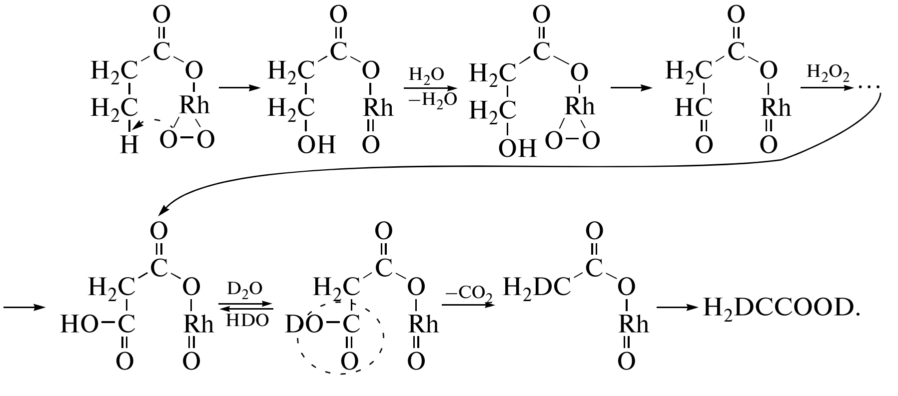
In the products of propionic acid oxidation in the deuterated solvent, deuterosubstituted acetic acids were found, which contain one or two D atoms in the methyl group. This is indicated by signals at *m/z* 62 (CH_2DCOOD or CHD_2COOH) and *m/z* 63 (CHD_2COOD or CD_3COOH) comparable in intensity with the signal of the molecular ion of acetic acid (*m/z*) 60) in the mass spectrum averaged over the chromatographic peak. Moreover, the signal intensities at *m/z* 44 (CO_2 and CH_2DCO) and *m/z* 45 (COOH and CHD_2COO) in the mass spectrum of acetic acid obtained in the oxidation of propionic acid are substantially higher than the intensities of these signals in the standard spectrum of CH_3COOH (Fig. 6a).

The methyl propionate molecular ion cluster found in the reaction products consists of ions having *m/z* 88, 89, and 90 with comparable intensities. The spectrum of the reaction product practically coincides with the tabulated spectrum of methyl propionate in the range of *m/z* 29–32 ($C_2H_5^+$ fragment ion) (Fig. 6b). These two observations indicate that methyl propionates differing by the depth of deuteration contain the deuterium atoms only in the methoxy group.

In the mass spectrum of methyl acetate found in the products of propionic acid oxidation, ions at *m/z* 43, 44, 45, and 46 were found in the cluster of acetyl ions, indicating the deuteration of the acetyl moiety of the ester molecule. Ions from $M^{+\bullet}$ to $(M + 6)^{+\bullet}$ were found in the cluster of the molecular ion, thereby indicating the presence of D atoms both in the acetyl and methoxy groups of the molecule (Fig. 6c).

In the absence of dioxygen, only the carboxylic hydrogen atoms of acetic and propionic acids are exchanged by deuterium. The H–D exchange was not observed in the methyl acetate and methyl propionate introduced into the solution. All these facts cannot be rationalized within the framework of the mechanism suggested above. According to this mechanism, the shortening of the carboxylic acid carbon chain occurs as a result of oxidative decarbonylation. The formation of deuterosubstituted acetic acids during the oxidation of propionic acid in D_2O can indicate the existence of the route that involves the methyl or the methylene group.

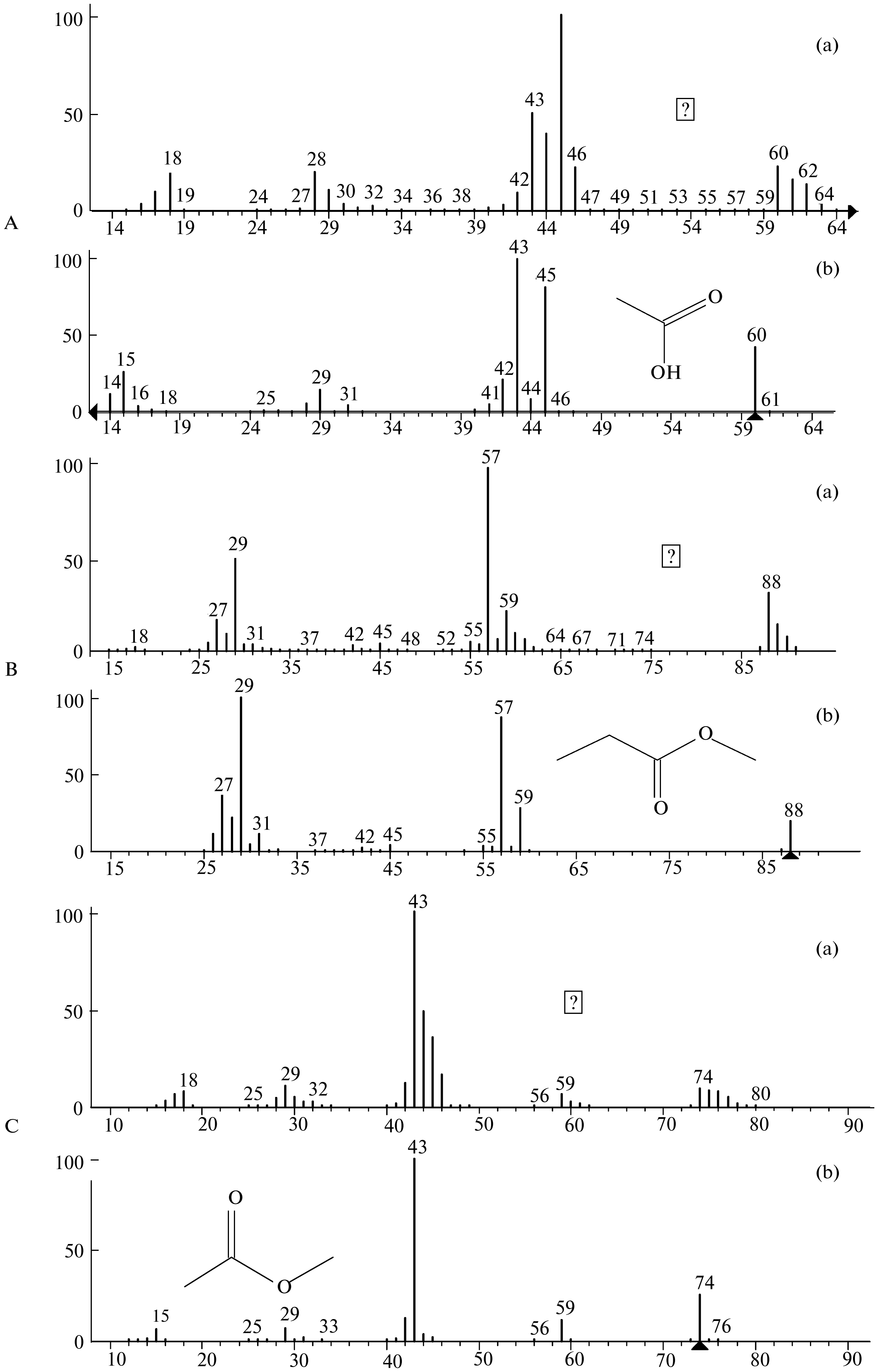
We cannot rule out that the coordinated propionate ion can be subjected to the inner-sphere oxidation by the action of the peroxo group coordinated at the rhodium atom [16]. The decarboxylation of the intermediate malonate in the proton-donating medium gives CDH_2COOD:



The possibility of the oxidation of propionic acid into acetic acid via the intermediate formation of 3-oxypropionic and malonic acids agrees with the published data [23] on the oxidation of labeled $CH_3CH_2{}^{13}COOH$; acetic acid $CH_3{}^{13}COOH$ is formed by the action of O_2 and CO in the presence of Pd/C–$CuCl_2$ in aqueous CF_3COOH. The formation of CD_2HCOO– and CD_3COO groups can be accounted for by the exchange of the methylene hydrogen atoms of malonic acid for deuterium [24].

The presence of methyl propionate deuterated in the methoxy group in the reaction products suggests

Fig. 6. Chromato-mass spectra of the products of propionic acid oxidation in the presence of D_2SO_4 (0.2 M) and D_2O (7 M): (A) the experimental peak of acetic acid (a) and the standard spectrum of acetic acid (b), (B) the experimental peak of methyl propionate (a) and the standard spectrum of methyl propionate (b), and (C) the experimental peak of methyl acetate (a) and the standard spectrum of methyl acetate (b); $[RhCl_3] = 2.5 \times 10^{-3}$ mol l^{-1}, $[Cu^{II}] = 5.0 \times 10^{-2}$ mol l^{-1}, $[NaCl] = 7.5 \times 10^{-3}$ mol l^{-1}, $[H_2O] = 7.0$ mol l^{-1}, He = 6 MPa, CO = 1.84 MPa, $O_2 = 0.56$ MPa, $T = 95°C$, 2 h.


A
(a)
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14 19 24 29 34 39 44 49 54 59 64
(b)
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42
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OH
O
14 19 24 29 34 39 44 49 54 59 64
B
(a)
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15 25 35 45 55 65 75 85
(b)
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45
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57
59
88
O
O
15 25 35 45 55 65 75 85
C
(a)
?
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18
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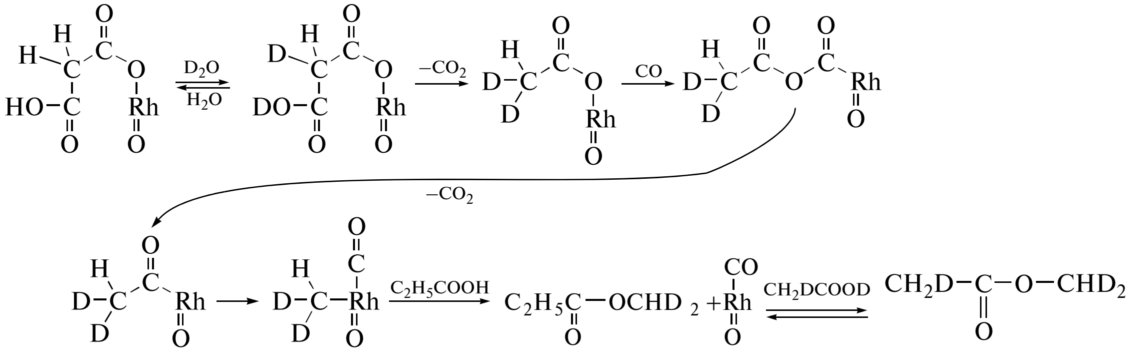
32
43
56
59
74
80
10 20 30 40 50 60 70 80 90
(b)
100
50
0
15
25
29
33
43
56
59
74
76
O
O
10 20 30 40 50 60 70 80 90

that deuterosubstituted methanols are formed as a result of oxidative decarboxylation of acetic acids deuterosubstituted in the methyl group according to the mechanism with participation of CO described above:



If this assumption is true, the ratio of the ion intensities corresponding to DH_2CO^+ and H_3CO^+ in the averaged mass spectrum of methyl acetate should coincide with the ratio of the ion intensities of $C_2H_5COOCH_2D^{+\bullet}$ and $C_2H_5COOCH_3^{+\bullet}$ in the averaged mass spectrum of methyl propionate[5]. The following values were obtained for the intensity ratios: $I_{DH_2CO^+}/I_{H_3CO^+} = 0.48$ and $I_{C_2H_5COOCH_2D}/I_{C_2H_5COOCH_3^{+}} = 0.46$.

Thus, the oxidative functionalization of methane in the rhodium–copper–chloride catalytic system by the action of O_2 and CO substantially depends on the solvent nature and its efficiency decreases in the order $CF_3COOH–H_2O > CH_3COOH–H_2O \gg C_2H_5COOH–H_2O$. Moreover, the solvents, namely acetic and propionic acids, are not inert and are subjected to oxidative transformations. Propionic acid blocks the methane oxidation.

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[5] It is incorrect to compare the ratios of ion intensities for di- and trideuterosubstituted esters, because of the effect of deuterium on the formation of the methoxy group.

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