

Uncommon oxidative transformations of acetic and propionic acids

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The oxidative decarbonylation of acetic and propionic acids with the formation of the corresponding alcohol and alkyl carboxylate is observed in the $\text{Rh}^{\text{III}}/\text{Cu}^{\text{I,II}}/\text{Cl}^-$ catalytic system in the presence of O_2 and CO . The decarbonylation of propionic acid in a deuterated solvent results in the substitution of hydrogen atoms by deuterium in the alkyl part of the products to form CH_2DCOOD (CHD_2COOH) and CHD_2COOD (CD_3COOH). The subsequent decarbonylation of deuterated acetic acids affords the corresponding deuteromethanols detected as esters with propionic and deuterioacetic acids. The substitution of the hydrogen atom by deuterium in the alkyl part of molecules of the products of oxidative decarbonylation of propionic acid, when the reaction is carried out in a deuterated solvent, indicates that propionic acid behaves as saturated hydrocarbon and blocks the oxidation of poorly soluble methane. Unlike propionic acid, acetic acid enters only the oxidative decarbonylation reaction and does not block methane oxidation.

Key words: methane, acetic and propionic acids, oxidation, rhodium and copper compounds.

Interest in chemistry of carboxylic acids is generated by their role of biomass treatment aimed at producing diesel fuel. The presence of the carboxyl group decreases the energy content of the fuel. Therefore, one of the problems, namely, removal of the carboxyl group from fatty acids of lipids, can be solved by the decarbonylation of the acid followed by the dehydration of the alcohol.¹ In the present work, the decarbonylation of propionic and acetic acids under mild conditions (95 °C) was studied. It has previously² been found that the decarbonylation of stearic acid on the rhodium catalysts occurs only at 240–280 °C.

Experimental

The following reagents and materials were used: $\text{RhCl}_3 \cdot (\text{H}_2\text{O})_n$ (34.5 wt.% Rh), NaCl, CuO, NaCl, H_2SO_4 , and HClO_4 (reagent grade), as well as H_2O (bidistillate). Acetic acid (reagent grade) was distilled, $\text{C}_2\text{H}_5\text{COOH}$ (Merck) was used as received, heptane (standard) was distilled off, and dioxane (reagent grade) was refluxed for 2 h above metallic sodium and then distilled. Methane (99.8%), carbon monoxide (99.9%), oxygen (99.9%), helium (trade mark A), nitrogen (special purity grade), hydrogen (99.0%), and deuterated compounds D_2O (99.9 at.%), CD_3COOD (99.5 at.%), and D_2SO_4 (98.0 at.%) were used without purification; and CD_4 (98.2 at.%) was condensed twice

* Dedicated to Academician S. N. Khadzhiev on the occasion of his 70th birthday.

at the temperature of liquid nitrogen and then evaporated at $-(60-50)$ °C to remove heavy admixtures, for instance, CCl_4 .

Catalytic experiments were carried out in a 34-cm³ Fluoroplast-lined stainless steel reactor using the earlier described procedure.^{3,4} In a typical experiment on methane oxidation, an autoclave was loaded with $6.25 \cdot 10^{-3}$ mmole of RhCl_3 and $18.75 \cdot 10^{-3}$ mmole of NaCl as solutions (0.25 g) in D_2O ; $[\text{RhCl}_3] = 2.5 \cdot 10^{-3}$ mol L⁻¹ and $[\text{NaCl}] = 7.5 \cdot 10^{-3}$ mol L⁻¹. Then a $0.96 \cdot 10^{-3}$ M D_2SO_4 solution (0.25 g) in D_2O , 2.27 g of CD_3COOD , and 10 mg of CuO were added. The autoclave was fed with the following gases: methane (6.0 MPa), oxygen (0.56 MPa), and carbon monoxide (1.84 MPa). The time of the experiment was 2 h. In a typical experiment on the oxidation of propionic acid, the autoclave was loaded with CuO (10 mg) and a solution (25 mL) prepared as follows: H_2O (1.4 mL), a solution of H_2SO_4 in H_2O ((0.56 mL, 3.9 mol L⁻¹), and $\text{C}_2\text{H}_5\text{COOH}$ (17 mL) were added to an aqueous solution (1.0 mL) containing RhCl_3 ($5 \cdot 10^{-2}$ mol L⁻¹) and NaCl (0.15 mol L⁻¹). The gases were fed in the following order: helium (4 MPa), oxygen (0.56 MPa), carbon monoxide (1.84 MPa), and again helium to a total pressure of 8.4 MPa. The duration of the experiment was 2 h.

The gas phase was analyzed by GC using the known procedure,^{3,4} and the liquid phase was analyzed by GC (flame ionization detector, N_2) on a Chrom-5 chromatograph with glass packed columns (inner diameter 2.5 mm). To determine the oxidation products of acetic acid, Separon CHN was used (0.115–0.200 mm, 2 m, 130 °C, dioxane as an internal standard), and propionic acid was determined on Separon SDA (2.4 m, 140 °C, heptane as an internal standard). The products

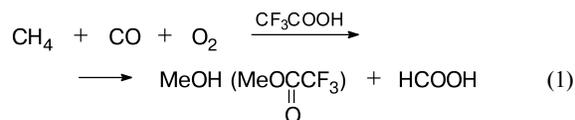
of oxidation of CH₄ in CD₃COOD/D₂O were analyzed by ¹H NMR on Bruker AC-200 P (200 MHz) and Tesla BS-587-A (80 MHz) instruments. An admixture of CHD₂COOD in CD₃COOD was used as an internal standard for quantitative measurements.

The initial ratio CH₄/CD₄ was determined by mass spectrometry on an MI-1201 instrument with a needle valve as a leak (pressure in the forecylinder 10⁻¹ Torr, electron impact 70 eV, ionization current 0.2 mA). The GC/MS experiment was carried out on an Automass 150 instrument (Delsi—Nermag) with a DN200 gas liquid chromatograph (Delsi), chromatographic column CPSil-5 (25 m × 0.15 mm), d_f = 1.2 μm (Chromopack), He as a carrier gas, constant pressure regime 1.2 bar, flow splitting injector 1 : 50, T_{inj} = 220 °C, temperature-programmed column T_{init} = 40 °C (4 min), T_{fin} = 250 °C (4 min), 10 °C min⁻¹. The ionization regime was as follows: electron impact, 70 eV, and resolution at least 2.0 M (M = m/z) in the range m/z 18–131. For the analysis of the isotopic composition, the spectra were recorded in the scanning mode in the range 15–100 m/z with scanning duration 100 ms. The Lucy ver. 2.0 and AMDIS ver. 2.62 program packages were used for processing GC/MS experiments. For sampling, the reaction solution was placed in a tube sealed with a chromatographic diaphragm. The tube was heated to ~60 °C, and then a gas sample was taken above the solution using a chromatographic syringe heated to ~50 °C. A gas sample (50–100 μL) was injected into the chromatograph.

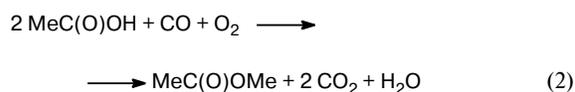
Results and Discussion

Homogeneous systems Rh^{III}/I⁻/Cl⁻, Rh^{III}/Cu^{I,II}/Cl⁻, and Rh^{III}/Fe^{II,III}/Cl⁻ manifest high catalytic activity in the direct oxidation of methane with oxygen. The neces-

sary component of the catalytic system in aqueous trifluoroacetic acid is CO.^{3–5} The initial activity of these systems at 95 °C and pressures (MPa, in parentheses) of CH₄ (6.0), CO (1.84), and O₂ (0.56) reaches 100–150 moles of CH₄ (mole of Rh)⁻¹ h⁻¹. The oxidation of CH₄ in the Rh^{III}/Cu^{I,II}/Cl⁻ system in a solution of CF₃COOH (see Ref. 4) affords the following products:



The replacement of the solvent by an aqueous solution of acetic acid (both with and without additives of sulfuric acid*) results in methane oxidation (Table 1, entries 1–3) and also (unexpectedly) the decarbonylation of acetic acid by reaction (2).



Free radicals make no substantial contribution to methane oxidation under our experimental conditions.⁶ In the absence of CO, neither methane nor the acid are involved in the reactions.

* Sulfuric acid was added to the solution in some experiments with acetic and propionic acids in order to mimic CF₃COOH.

Table 1. Catalytic oxidative functionalization of methane in aqueous acetic and propionic acids^a

Entry	Organic acid	Water (C/mol L ⁻¹)	Concentration of H ₂ SO ₄ /mol L ⁻¹	Methane ^b	Products ^c
1 ^d	CH ₃ COOH	H ₂ O (8.0)	0.20	CH ₄ : CD ₄ = 0.76	CH ₃ COOCH ₃ —CH ₃ COOCD ₃ (78 : 1)
2	CD ₃ COOD	D ₂ O (17.1)	—	CH ₄	CD ₃ COOCD ₃ —CD ₃ COOCH ₃ (1.83 : 1)
3	CH ₃ COOH	H ₂ O (16.0)	—	CD ₄	CH ₃ COOCH ₃ —CH ₃ COOCD ₃ (17.5 : 1)
4	CH ₃ COOH	H ₂ O (7.0)	0.20	0 ^e	CH ₃ COOCH ₃ (3.1 · 10 ⁻² mol L ⁻¹)
5	C ₂ H ₅ COOH	H ₂ O (7.0)	0.10	CH ₄	C ₂ H ₅ COOCH ₃ —C ₂ H ₅ COOC ₂ H ₅ (1.9 : 1)
6	C ₂ H ₅ COOH	H ₂ O (7.0)	0.11	0 ^e	C ₂ H ₅ COOCH ₃ —C ₂ H ₅ COOC ₂ H ₅ (1.7 : 1)
7	C ₂ H ₅ COOH	H ₂ O (16.0)	—	CD ₄	C ₂ H ₅ COOCH ₃ , C ₂ H ₅ COOC ₂ H ₅
8	C ₂ H ₅ COOH	H ₂ O (7.0)	0.10	CD ₄	C ₂ H ₅ COOCH ₃ , C ₂ H ₅ COOC ₂ H ₅

^a [RhCl₃] = 2.5 · 10⁻³ mol L⁻¹, [NaCl] = 7.5 · 10⁻³ mol L⁻¹, [Cu^{I,II}] = 5 · 10⁻² mol L⁻¹, T = 95 °C, P_{O₂} = 0.56 MPa, P_{CO} = 1.84 MPa, 2 h.

^b CH₄ (6.0 MPa), CD₄ (4.0 MPa) + He (2.0 MPa).

^c The quantitative composition and the ratio were determined by the GC/MS method.

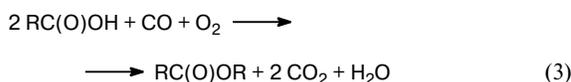
^d The reaction time is 1 h.

^e Methane was replaced by helium.

It was found that under the experimental conditions used the amount of methyl acetate exceeds the amount of the loaded catalyst (rhodium) by at least an order of magnitude. Methyl acetate is formed both in the presence of methane (see Table 1, entries 1–3) and without it (see Table 1, entry 4). Thus, methane is not the single source of methanol and its ester. At least a portion of these products is formed from a component of the solvent, *viz.*, acetic acid.

Methyl propionate, ethyl propionate, ethyl chloride, and acetic and formic acids were identified in an aqueous solution of propionic acid acidified with sulfuric acid both in the presence and in the absence of methane in the catalytic system $\text{Rh}^{\text{III}}/\text{Cu}^{\text{I,II}}/\text{Cl}^-$. When methane is replaced by helium, methyl propionate and ethyl propionate are formed in almost the same ratio (see Table 1, entries 5 and 6).

No transformations of acetic or propionic acid are observed in the experiments, where helium, helium + oxygen, and helium + carbon monoxide were used as the gas phase. Thus, the necessary condition for the decarbonylation of the studied carboxylic acids (reaction (3)) is the presence of both CO and O_2 .



R = Me, Et

Additives of sulfuric acid decrease the probability of the nucleophilic attack of water or reduce the concentration of the rhodium or copper oxo complexes and increase the yield of decarbonylation products (Fig. 1, curves 1 and 3). Similar inhibition of olefin oxidation by the acid in the

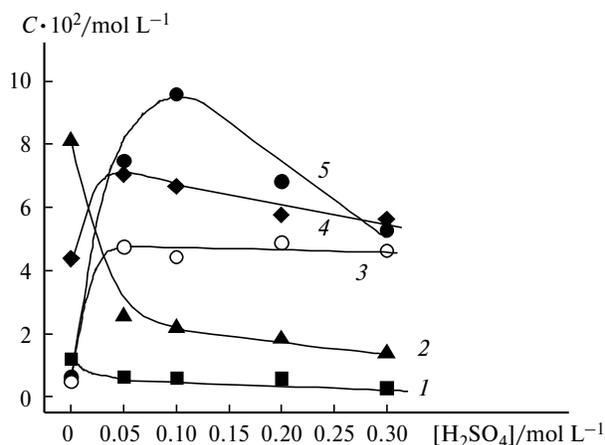


Fig. 1. Yield of the products of propionic acid transformation vs concentration of H_2SO_4 : EtOH (1), MeOH (2), EtCOOC $_2$ H $_5$ (3), MeCOOH (4), and EtCOOCH $_3$ (5). Small amounts of methyl acetate are also observed (omitted). Conditions: $[\text{RhCl}_3] = 2.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{Cu}^{\text{II}}] = 5.0 \cdot 10^{-2} \text{ mol L}^{-1}$, $[\text{NaCl}] = 7.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}] = 7.0 \text{ mol L}^{-1}$, $P_{\text{He}} = 6 \text{ MPa}$, $P_{\text{CO}} = 1.84 \text{ MPa}$, $P_{\text{O}_2} = 0.56 \text{ MPa}$, $T = 95 \text{ }^\circ\text{C}$, 2 h.

presence of the palladium complexes is due to the protonation of the hydroxyl group coordinatively bound in the π -palladium complex.⁷ On the one hand, an increase in the water concentration favors the oxidation of CO (reaction (4)) and, on the other hand, it decreases the yield of the decarbonylation products of propionic acid, ethanol and ethyl propionate (Fig. 2, curves 2 and 7).



This indirectly confirms the existence of the same intermediate in the oxidative decarbonylation of carboxylic acids and CO oxidation.

The oxidation of CD_4 in propionic acid (with and without sulfuric acid additives) affords no deuterated products* (see Table 1, entries 7 and 8). The absence of deuterated products of the oxidation of CD_4 in the studied system indicates that methane does not participate in the formation of methyl propionate. This means that, unlike solutions of acetic acid, no methane oxidation occurs in solutions of propionic acid. All identified products with the carbon chain shorter than that of propionic acid are formed by the oxidative decarbonylation of propionic acid.

The formation of acetic acid, methanol, and methyl propionate from propionic acid cannot be considered as

* The analytical procedures used in the work would make it possible to determine deuterated methyl propionate in the concentration down to $10^{-3} \text{ mol L}^{-1}$.

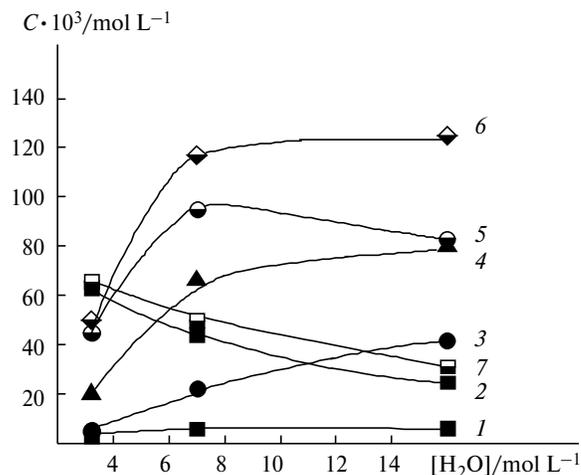


Fig. 2. Influence of the H_2O concentration on the yield of the oxidation products of propionic acid: C $_2$ H $_5$ OH (1), C $_2$ H $_5$ COOC $_2$ H $_5$ (2), CH $_3$ OH (3), CH $_3$ COOH (4), C $_2$ H $_5$ COOCH $_3$ (5), CH $_3$ OH + C $_2$ H $_5$ COOCH $_3$ (6), and C $_2$ H $_5$ OH + C $_2$ H $_5$ COOC $_2$ H $_5$ (7). Small amounts of methyl acetate are also observed (omitted). Conditions: $[\text{RhCl}_3] = 2.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{Cu}^{\text{II}}] = 5.0 \cdot 10^{-2} \text{ mol L}^{-1}$, $[\text{NaCl}] = 7.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 0.1 \text{ mol L}^{-1}$, $P_{\text{He}} = 6 \text{ MPa}$, $P_{\text{CO}} = 1.84 \text{ MPa}$, $P_{\text{O}_2} = 0.56 \text{ MPa}$, $T = 95 \text{ }^\circ\text{C}$, 2 h.

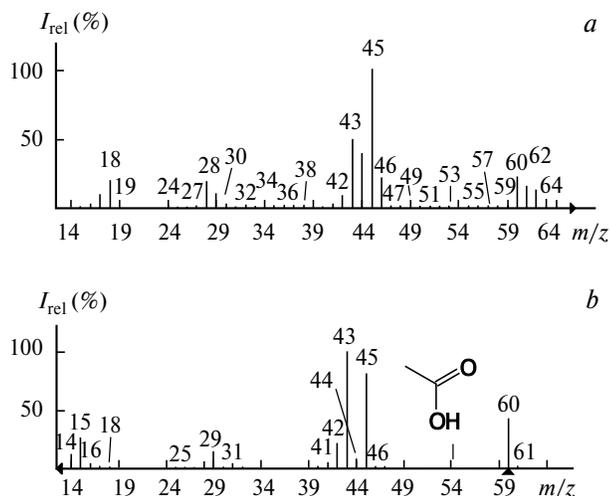


Fig. 3. Mass spectra of the chromatographic peak at 6.7–7.1 min (a) and the reference spectrum of acetic acid (b).

the successive transformation $C_2H_5COOH \rightarrow C_2H_5OH \rightarrow CH_3COOH$ and the further decarbonylation of CH_3COOH , since the combined oxidation of propionic

acid and C_2D_5OD affords no CD_3COOH . Therefore, acetic acid is not a product of ethanol oxidation, which is formed due to the oxidative decarbonylation of propionic acid.

Under conditions described above, deuterated acetic acids containing one and two D atoms in the methyl group were found among the oxidation products of propionic acid in the presence of D_2SO_4 (0.2 mol L^{-1}) and D_2O (7.0 mol L^{-1}) (see Fig. 1). This is indicated by the signals with m/z 62 (CH_2DCOOD or CHD_2COOH) and 63 (CHD_2COOD or CD_3COOH), whose intensity is comparable with that of the signal of the molecular ion of acetic acid (m/z 60) in the mass spectrum* (Fig. 3, a) averaged by the chromatographic peak at 6.7–7.1 min (Fig. 4). In addition, the intensities of the signals with m/z 44 (CO_2 and CH_2DCO) and 45 ($COOH$ and CHD_2COO) in the mass spectrum of acetic acid obtained by the oxidation of propionic acid are substantially higher than the intensities of the same signals in the reference spectrum of CH_3COOH (Fig. 3, b).

* The mass spectrum was recorded in each point (with a frequency of $\sim 5 \text{ s}^{-1}$) of the chosen region of the chromatogram. The final mass spectrum is weighed average.

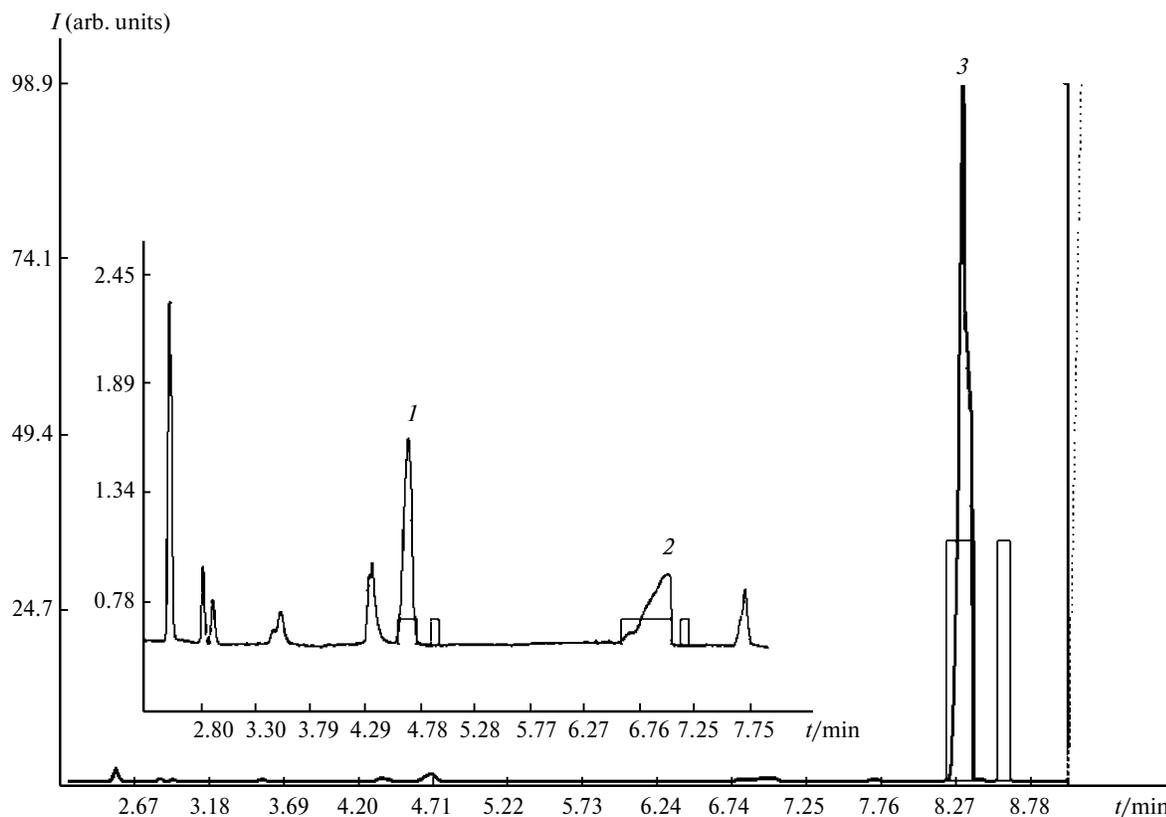


Fig. 4. Chromatogram of the oxidation products of propionic acid in the presence of D_2SO_4 (0.2 mol L^{-1}) and D_2O (7.0 mol L^{-1}): methyl acetate (1), acetic acid (2), and methyl propionate (3). Conditions: $[RhCl_3] = 2.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[Cu^{II}] = 5.0 \cdot 10^{-2} \text{ mol L}^{-1}$, $[NaCl] = 7.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $P_{He} = 6 \text{ MPa}$, $P_{CO} = 1.84$, $P_{O_2} = 0.56 \text{ MPa}$, $T = 95 \text{ }^\circ\text{C}$, 2 h. Rectangles designate regions of averaging the chromatographic signals of the product and background; I is the total ionic current.

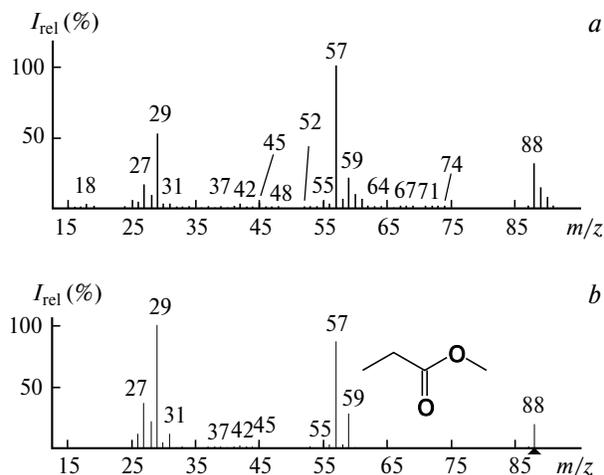


Fig. 5. Mass spectra of the chromatographic peak at 8.46 min (*a*) and the reference spectrum of methyl propionate (*b*).

The cluster of the molecular ion of methyl propionate found in the reaction products (peak at 8.46 min in the chromatogram, see Fig. 4) consists of ions with m/z 88, 89, and 90 with the comparable intensity. In the region of m/z 29–32 (fragmentation ion $C_2H_5^+$), the spectrum of the reaction product almost coincides with the tabulated spectrum of methyl propionate (Fig. 5, *b*). Both these facts indicate that the methyl propionates formed contain deuterium atoms only in the methoxy groups.

The mass spectrum of methyl acetate found among the oxidation products of propionic acid exhibits ions with m/z 43, 44, 45, and 46 (Fig. 6, *a*) in the cluster of the acetyl ion, indicating the deuteration of the acetyl moiety of the ester molecule. The cluster of the molecular ion contains ions from $[M]^+$ to $[M + 6]^+$, which shows the

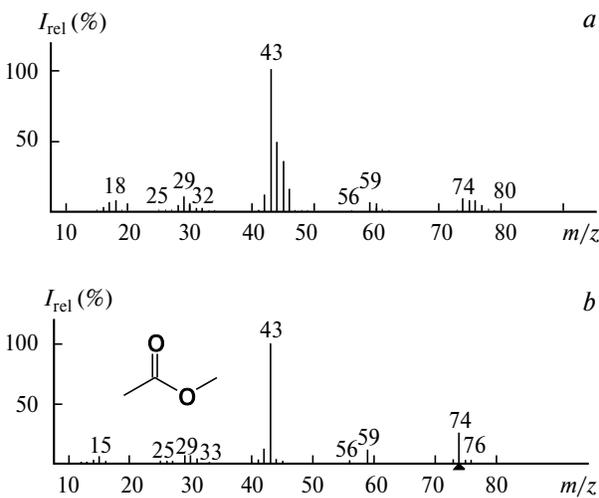


Fig. 6. Mass spectra of the chromatographic peak at 4.67 min (*a*) and the reference spectrum of methyl acetate (*b*).

presence of atoms D in both the acetyl and methoxy group of the molecule (see Fig. 6).

In the absence of oxygen, only the hydrogen atom of the carboxyl group in acetic and propionic acids is replaced by deuterium, while no H–D exchange occurs in the presence of methyl acetate and methyl propionate added to the system. Based on all these facts, the deuterio-substituted acetic acid derivatives are formed by the oxidation of propionic acid in the deuterated solvent, which involves the methyl groups.

The presence of methyl propionates deuterio-substituted at the methoxy group in the reaction products suggests that deuterio-substituted methanols are formed due to the oxidative decarbonylation of the acetic acid derivatives deuterio-substituted at the methyl group involving CO and O_2 . If this assumption is valid, the ratio of peak intensities corresponding to the ions DH_2CO^+ and H_3CO^+ of methyl acetate should coincide with the ratio of peak intensities of the ions $C_2H_5COOCH_2D^+$ and $C_2H_5COOCH_3^+$ in the averaged mass spectrum of methyl propionate (for di- and trideuterio-substituted esters, the comparison of the ratios of ion intensities is incorrect because of the kinetic isotopic effect of methoxy group formation). In experiment $I_{DH_2CO^+}/I_{H_3CO^+} = 0.48$ and $I_{C_2H_5COOCH_2D^+}/I_{C_2H_5COOCH_3^+} = 0.46$ were obtained.

Thus, it was found in the present work that the oxidative decarbonylation of acetic and propionic acids to methanol (methyl acetate) and ethanol (ethyl propionate), respectively, occurs during the combined oxidation of carboxylic acids and CO in the presence of the rhodium catalyst. The unusual substitution of deuterium for hydrogen atom in the alkyl part of molecules of the products of propionic acid oxidative carbonylation was also observed. Propionic acid, whose methyl group is separated from the electron-acceptor carboxyl group, behaves similarly to unsaturated hydrocarbon and competes with poorly soluble methane in the reaction with the reactive intermediate. The formation of the deuterio-substituted products with the carbon chain smaller than that in the initial acid is due to the oxidation of the methyl group. Unlike propionic acid, acetic acid is involved only in the oxidative decarbonylation reaction and does not block methane oxidation.

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