Direct Catalytic Oxidation of Lower Alkanes in Ionic Liquid Media

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Abstract—Immobilization of rhodium (palladium)–copper–chloride catalytic systems in ionic liquids as high-boiling-point solvents affects the distribution of propane oxidation products: the acetone yield increases and the yield of alcohols decreases. Propane is oxidized to acetone, bypassing the isopropanol formation step. Methane is oxidized under more severe conditions than propane, giving methyl trifluoroacetate as the main product. Mechanisms of action of the catalytic systems based on rhodium and palladium are close to each other and likely include oxo or peroxo complexes as intermediates.

The problem of the direct oxidation of alkanes in the presence of metal complex catalysts is related to the activation of both C–H bond and molecular oxygen [1, 2]. The solution of this problem would facilitate the development of new technologies for processing natural gas and associated petroleum gas.

Previously, we developed rhodium- and palladium-containing catalytic systems and studied the mechanism of their operation [3–5]. The systems effectively operate in aqueous trifluoroacetic acid. To convert oxygen to an active two-electron oxidant, the reducing agent carbon monoxide is introduced. This process is enhanced by adding cocatalysts (reoxidant), such as iodine, iron, and copper compounds. In catalysis by rhodium or palladium complexes, the cocatalysts are reduced with carbon monoxide to a low-valence state, and they are capable of reacting with oxygen in this state. On the other hand, there are reasons to believe that the C–H bond in alkanes is activated on rhodium (palladium) oxo or peroxo complexes [5].

Attempts to replace trifluoroacetic acid by another, less toxic and less corrosive solvent failed. The catalytic systems in aqueous solutions of dioxane, tetrahydrofuran, and acetonitrile are inactive. Certain catalytic activity was observed in acetic acid, but acetic and propionic acids were found to undergo degradation under alkane oxidation conditions [6–8].

The objectives of this work were to determine whether it is possible to replace in part trifluoroacetic acid by any of high-boiling-point solvents including ionic liquids (ILs) and immobilize the catalytic system in these solvents, to study the influence of ILs on reaction selectivity, and to elucidate the acetone formation route.

EXPERIMENTAL

Materials

The reagent-grade chemicals $RhCl_3 \cdot (H_2O)_x$ (Rh 34.5 wt %), NaCl, and CuO; H_2O (bidistillate);and CF_3COOH (Aldrich 99%, extra pure) were used without further purification. Pyridine of the reagent grade was distilled, and analytical-grade H_3PO_4 had a concentration of 83.84 wt %. Dioxane (reagent grade) was refluxed for 2 h over sodium metal and distilled. Trifluoroacetic acid esters were prepared according to the procedure described in [9] and distilled. The purity of the products was controlled using GC and GC–MS methods. Copper(II) trifluoroacetate was obtained by dissolving CuO in CF_3COOH under refluxing, dried in vacuum after cooling, and stored in a desiccator. Isopropanol-^{18}O with an enrichment of 75% was obtained by hydrogenating acetone-^{18}O on Raney nickel. Acetone-^{18}O was obtained by hydrolysis of 2,2-dimethoxypropane (Aldrich 99%, extra pure) with $H_2^{18}O$ (enrichment ca. 80%). Gases were CO (99.9%), CH_4 (99.8%), C_3H_8 (99.8%), O_2 (99.9%), electrolytic H_2, and grade "A" helium.

Catalytic Experiments

The experiments were carried out in a 34-cm³ temperature-controlled stainless steel reactor lined with fluoroplastic. A contact solution was prepared in a special container. In a typical run (Fig. 1, a point at

[PyH$^+$Ac$_f$O$^-$]=2 mol/L), 0.25 mL of an aqueous solution of [RhCl$_3$] = 5 × 10^{-2} mol/L and [NaCl] = 0.15 mol/L, 0.23 mL of H$_2$O, 2.42 mL of CF$_3$COOH, and 0.4 g (5 mmol) of pyridine were placed in the container. Pyridinium trifluoroacetate [PyH$^+$Ac$_f$O$^-$] forms in situ to consume 0.4 mL of CF$_3$COOH. The amounts of the components to be introduced were controlled on an analytical balance for greater accuracy; then, the contents of the container was charged to the reactor in which a weighed portion of copper trifluoroacetate (0.0725 g, 0.25 mmol) had been already placed. The reactor was sealed, and gases were fed: CH$_4$ = 6.0 MPa, O$_2$ = 0.8 MPa, and CO = 1.6 MPa. Propane was dosed from a graduated gas burette by means of liquefaction with liquid nitrogen in a special condenser installed before the reactor. After thawing, the condenser was connected with the reactor and the gases were fed through the condenser at He = 4.0 MPa, O$_2$ = 0.8 MPa, and CO = 1.6 MPa. A 10-MPa standard pressure gage having a division value of 0.04 MPa was mounted in the gas line for accurate gas dosage. After supplying the gases, the reactor valve was closed, jointed with a thermostat preliminarily heated up to a reaction temperature, and agitation was turned on. After the run was completed, the reactor was cooled with tap water to ≈12°C and the gas phase was released into an evacuated ~2-L glass flask. The gas phase and the liquid catalyzate were analyzed using GC and GC−MS techniques. The concentrations of the catalytic system components and analysis results are given in the tables and figures.

Analysis

The gas phase was analyzed on a Model 3700 chromatograph (Khromatograf pilot plant, Moscow) at 55°C with a thermal conductivity detector and helium as the carrier gas. Columns: 5 Å molecular sieves with a particle size of 0.2−0.3-mm, l = 3 m, d = 3 mm, He = 30 mL/min (O$_2$, N$_2$, CH$_4$, CO); Porapak Q with a particle size of 0.115−0.200-mm, l = 2m, d = 2.5 mm, He = 20 mL/min (CO$_2$, propane).

The liquid phase was analyzed on a Kristallyuks 4000M gas chromatograph with a flame-ionization detector, using a NetChrom V2.1 program and a CP-Sil 5CB Agilent capillary column, l = 25 m, d = 0.15 mm, temperature programming from 40 to 150°C at a heating rate of 5°C/min, He = 20 mL/min, inlet pressure of 1.3 atm, and a split ratio of 1 : 70 to have a column flow rate of 0.287 mL/min. Sample preparation before injecting liquid samples into the vaporizer was practiced.

GC−MS measurements were made with a Delsi-Nermag Automass 150 instrument equipped with a DN200 gas chromatograph (Delsi). A CPSil 5 chromatographic column (25 m × 0.15 mm, d_f = 1.2 μm (Chrompack) was used. The carrier gas was He, constant pressure mode of 1.2 bar, an injector with a 1 : 50
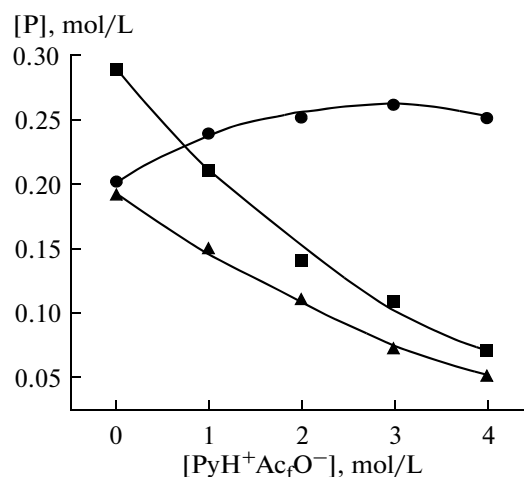

Fig. 1. The yield of propane oxidation products ([P]) in the presence of pyridinium trifluoroacetate on the rhodium−copper−chloride catalytic system in the CF$_3$COOH−H$_2$O medium: [RhCl$_3$] = 5 × 10^{-3} mol/L; Cu(Ac$_f$O)$_2$ = 1 × 10^{-1} mol/L, [NaCl] = 1.5 × 10^{-2} mol/L, m_{H_2O} = 0.5, T = 80°C, propane = 12 mmol, O$_2$ = 0.8 MPa, CO = 1.6 MPa, He = 4.0 MPa; 2.5 h: (●) acetone, (■) Ac$_f$OPr^i, and (▲) Ac$_f$OPr. Small amounts of methyl and ethyl trifluoroacetates (absent in graph) were also found.

split ratio was used, T_{inj} = 220°C, a temperature-programmed column was used, T_{start} = 40°C (4 min), T_{end} = 250°C (4 min), temperature rise was 10°C/min. The ionization mode was an electron impact of 70 eV, a resolution was no less than 2.0 M (where M is m/z) within 18−131 m/z range. To determine the isotope composition, the spectra were recorded in the scanning mode within the 15−100 m/z range; the scan time was 100 ms. The Lucy ver. 2.0 and AMDIS ver. 2.62 software suites were used for GC−MS data acquisition and processing. For sampling, the reaction mixture was placed into a test tube sealed with a membrane, heated up to ~60°C, and the headspace was sampled with a chromatographic syringe heated to ~50°C. The sample (50−100 μL) was introduced into the chromatograph.

Sample Preparation for GC and GC-MS Analyses

The non-demixing catalyzates containing internal standards were charged in a special reactor having a chromatographic silicone membrane (septum), and the reactor was thermostated at 50°C for 20 min. Then, the headspace was sampled with a gas syringe heated to 60°C. The sample injected into the chromatograph of a 100−150-μL size. Analysis was conducted in two steps. Firstly, methyl, ethyl, isopropyl,
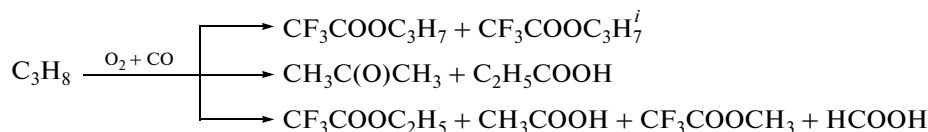
and propyl trifluoroacetates were determined with *n*-butyl trifluoroacetate as the internal standard. Then, the calculated amount of pyridine was introduced in the reactor under cooling to neutralize CF_3COOH, the reactor was thermostated for 1 h, and acetone and dioxane (internal standard) were determined. The demixing catalyzates, which are produced at high H_3PO_4 (phosphoric acid) concentrations, were preliminarily recondensed in a vacuum and then analyzed as described above. Trifluoroacetic acid neutralization leads to a sharp increase in sensitivity for acetone.

RESULTS AND DISCUSSION

Oxidation of Propane

Rhodium (palladium)−copper−chloride catalytic systems are some of the most effective systems for oxidation of C_1−C_4 alkanes. The process proceeds under the action of O_2−CO in the trifluoroacetic acid−water medium.

The oxidation of C_2−C_4 alkane involves not only C−H bond, but also C−C bond cleavage, as shown in scheme 1 using propane as an example [10, 11].

$$C_3H_8 \xrightarrow{O_2 + CO} \begin{cases} CF_3COOC_3H_7 + CF_3COOC_3H_7^i \\ CH_3C(O)CH_3 + C_2H_5COOH \\ CF_3COOC_2H_5 + CH_3COOH + CF_3COOCH_3 + HCOOH \end{cases}$$

Scheme 1. Propane oxidation.

Previously, we revealed the most likely routes for the formation of products with a shorter hydrocarbon chain compared with the substrate alkane [10, 11]. The possibility of the oxidation of isopropanol to acetone in the absence of propane was determined experimentally [10, 11]. However, it was unclear whether propane is oxidized directly to acetone, bypassing the isopropanol formation step, and what is the contribution of this reaction to the overall process. For example, it is known that in the case of cyclohexane oxidation with H_2O_2 on vanadium(V) [12], cyclohexanol and cyclohexanone were produced via different routes and cyclohexanol was not oxidized to cyclohexanone. In this connection, we attempt the investigation of propane oxidation in the presence of $^i Pr^{18}OH$. As follows from the data in Table 1, the simultaneous oxidation of both propane and $^i Pr^{18}OH$ with $^{16}O_2$ exceptionally results in $CH_3 - C(^{16}O) - CH_3$ regardless of the concentration of pyridinium trifluoroacetate taken as the IL. The same result was also obtained for 4-picolinium trifluoroacetate (Table 1, run 4). On the basis of these data, it can be concluded that propane is oxidized to acetone without the step of isopropanol formation. Moreover, the almost compete absence of $CH_3 - C(^{18}O) - CH_3$ in the catalyzates suggests that propane favored in competition with Pr^iOH for oxidation. It also follows from these data that the $Ac_f^{18}OPr^i / Ac_f^{16}OPr^i$ ratio (herein and hereinafter $Ac_f = CF_3CO$) increases with the pyridinium trifluoroacetate concentration.

This conclusion is consistent with the data in Fig.1: the yield of the esters drops with an increase in the pyridinium trifluoroacetate concentration. Note that the esters in this case are produced from both propane and admixed $^i Pr^{18}OH$, as well from $^i Pr^{16}OH$ remaining in $^i Pr^{18}OH$ because of the incomplete enrichment in ^{18}O. As a preliminary conclusion, it may be assumed that propane is oxidized by the high-valence rhodium peroxo complex in the concerted process when one oxygen atom forms water and the other adds to the carbon atom. Another possibility is the oxidative dehydrogenation of propane followed by propylene oxidation to acetone. The dehydrogenation of alkanes under oxidation conditions was reported in [13]. The available data allow us to refine the scheme of propane oxidation routes (Scheme 2).

Scheme 2 is based on the fact that we managed to accomplish almost all of the consecutive reactions. Route (a) leads to isopropanol (as ester) and acetone; acetone oxidation results in methanol (as ester), acetic acid, and formic acid. *n*-Propanol, which is in equilibrium with the ester, is oxidized to propionic acid. Propionic acid is oxidized via routes (b) and (c). By route (b), oxidation proceeds in the Rh coordination sphere. First, CO insertion in the Rh−OOCEt bond takes place, and the subsequent decarboxylation and decarbonylation give $\Sigma Rh - Et$. The final product is ethanol (as ester). By route (c), β-hydroxypropionic acid and then malonic acid are produced. When the reaction is run in a deuterated medium ($CF_3COOD - D_2O$), proton exchange in malonic acid takes place and the subsequent decarboxylation of $DOOC - CH_2 - COOD$ leads to the DCH_2COOD detected [11].

Table 1. Combined propane and isopropanol-^{18}O oxidation in the presence of the rhodium–copper–chloride catalytic system in the $CF_3COOH–H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $[Cu(Ac_fO)_2] = 1 \times 10^{-1}$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L, propane = 12 mmol, CO = 1.6 MPa, $^{16}O_2 = 0.8$ MPa, He = 4.0 MPa; $T = 80°C$, $m_{H_2O} = 0.5$ (m_{H_2O} herein and hereinafter is the molar fraction of water with respect to trifluoroacetic acid). Isotopic enrichment of $^iPr^{18}OH$ is 75%

No.	Run time, h	IL, mol/L	$[^iPr^{18}OH]$, mol/L	Reaction products [a]				
				GC analysis			GC–MS analysis	
				$[Ac_fOPr^i]$, mol/L	$[Ac_fOPr]$, mol/L	[acetone], mol/L	$\left[\dfrac{Ac_f^{18}OPr^i}{Ac_f^{16}OPr^i}\right]$	$\dfrac{CH_3-C(^{18}O)CH_3}{CH_3-C(^{16}O)CH_3}$
1	2.0	0	0.33	0.556	0.194	0.215	0.63	0.0065
2	2.5	$[PyH^+Ac_fO^-]$ 1.5	0.32	0.313	0.088	0.285	0.94	0.0068
3	2.5	$[PyH^+Ac_fO^-]$ 3.1	0.34	0.285	0.048	0.259	1.59	0.0058
4	2.5	$[4\text{-}PicH^+Ac_fO^-]$ 3.0	0.37	0.316	0.021	0.124	2.54	0.0055

[a] There are also methyl, ethyl, and isopropyl trifluoroacetates, acetic and propionic acids in reaction products.
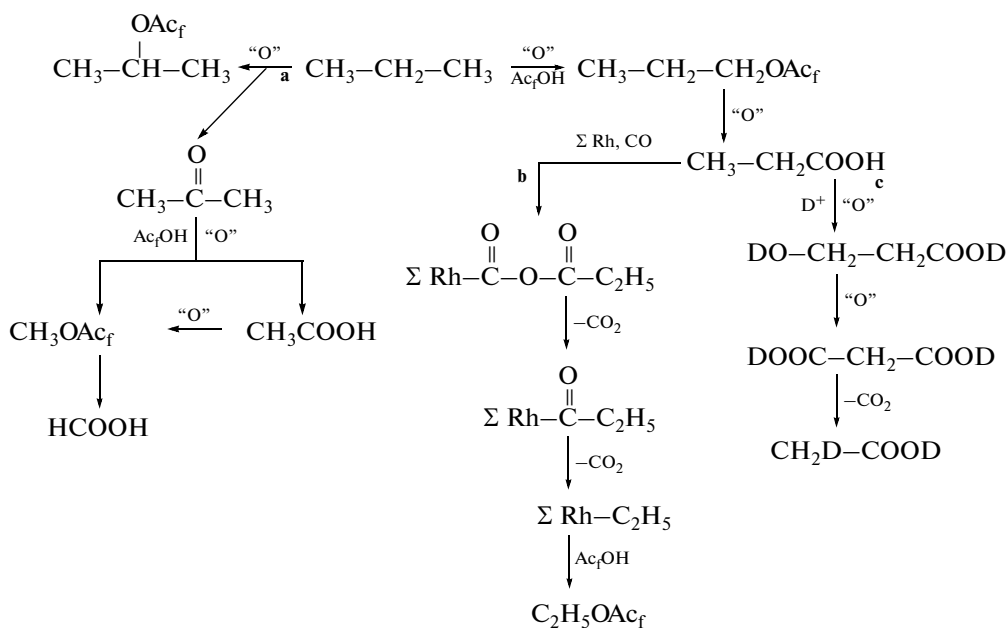
Scheme 2. Routes of propane oxidation to intermediate and final products. "O" is the active oxidant, ΣRh is the rhodium complexes in the ligand environment (esters are in equilibrium with alcohols, with the equilibrium being shifted to the ester side).

According to the work objectives, the influence of N-methylimidazolinium tetrafluoroborate ($MIMH^+BF_4^-$), N-methylimidazolinium trifluoroacetate ($MIMH^+Ac_fO^-$), pyridinium trifluoroacetate ($PyH^+Ac_fO^-$), and picolinium trifluoroacetate ($4\text{-}PicHAc_fO^-$) on propane oxidation was investigated. It was found that in the presence of the rhodium–copper–chloride catalytic system, an increase in the $MIMH^+BF_4^-$ concentration to 0.26 mol/L

leads to an increase in the acetone yield. A further increase in the $MIMH^+BF_4^-$ concentration decreases the yields of all products except formic acid (Table 2, runs 1–5).

Precipitates, presumably of rhodium and copper tetrafluoroborates, formed in this case. However, no precipitate appeared when $MIMH^+Ac_fO^-$ was used. An increase in the $MIMH^+Ac_fO^-$ concentration leads to a substantial increase in the acetone yield and a decrease in the esters yields of both n-propyl and iso-

Table 2. Propane oxidation in the presence of IL on the rhodium–copper–chloride catalytic system in the $CF_3COOH-H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $[Cu(Ac_fO)_2] = 1 \times 10^{-1}$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L, $m_{H_2O} = 0.5$, CO = 1.6 MPa, $O_2 = 0.8$ MPa, He = 4.0 MPa; $T = 80°C$, 3 h

No.	IL, mol/L	Propane, mmol	Products, mol/L					
			Ac_fOMe	$CH_3C(O)CH_3$	HCOOH	Ac_fOEt	Ac_fOPr	Ac_fOPr^i
1	0	12.0	0.04	0.09	0.22	0.08	0.17	0.31
2	$MIMH^+BF_4^-$ (0.1)	12.0	0.04	0.19	0.24	0.08	0.19	0.30
3	$MIMH^+BF_4^-$ (0.264)	12.0	0.01	0.21	0.33	0.05	0.16	0.21
4	$MIMH^+BF_4^-$ (0.51)	12.0	–	0.14	0.35	0.01	0.08	0.07
5	$MIMH^+BF_4^-$ (1.0)	12.0	–	0.06	0.43	–	0.02	0.02
6	0	24.0	0.02	0.09	0.18	0.06	0.21	0.27
7	$MIMH^+Ac_fO^-$ (0.29)	24.0	0.04	0.12	0.26	0.09	0.23	0.32
8	$MIMH^+Ac_fO^-$ (0.50)	24.0	0.04	0.13	0.33	0.07	0.20	0.28
9	$MIMH^+Ac_fO^-$ (0.81)	24.0	0.04	0.15	0.57	0.07	0.17	0.22
10	$MIMH^+Ac_fO^-$ (1.47)	24.0	0.03	0.20	0.63	0.05	0.15	0.19
11	$MIMH^+Ac_fO^-$ (1.93)	24.0	0.02	0.22	1.17	0.04	0.07	0.09
12	$PyH^+Ac_fO^-$ (1.98)	24.0	0.03	0.21	0.14	0.06	0.14	0.18
13	$4\text{-}PicH^+Ac_fO^-$ (2.0)	12.0	0.02	0.18	–	0.03	0.13	0.08
14	$4\text{-}PicH^+Ac_fO^-$ (4.0)	12.0	Traces	0.10	–	Traces	0.03	0.02

propyl alcohols. In addition, the catalyst color changed from green to brown, which can be due to the oxidative degradation of $MIMH^+Ac_fO^-$ (Table 2, runs 6−11). Also, the yield of formic acid significantly increases. Blank runs showed that propane was not a single source of formic acid (Table 3, runs 1−3).

Substitution of ^{13}CO for ^{12}CO showed that CO does not participate in the formation of formic acid (Table 3, run 4). The use of pyridinium trifluoroacetate $(PyH^+Ac_fO^-)$ and picolinium trifluoroacetate $(4\text{-}PicHAc_fO^-)$ as IL did not results in formic acid in blank runs (Table 3; runs 5, 6). It follows from

Table 3. Results of blank runs (in the absence of propane) under conditions of runs of Table 2

No.	IL, mol/L	HCOOH, mol/L
1	–	0.0
2	$MIMH^+Ac_fO^-$ (0.5)	0.16
3	$MIMH^+Ac_fO^-$ (2.05)	1.60
4[a]	$MIMH^+Ac_fO^-$ (0.51)	$H^{12}COOH$ 0.15
5	$PyH^+Ac_fO^-$ (0.51)	0.0
6	$4\text{-}PicH^+Ac_fO^-$ (0.50)	0.0

[a] $^{13}CO = 1.6$ MPa was introduced.

these facts that formic acid is produced in oxidation of N-methylimidazole in the runs with $MIMH^+Ac_fO^-$. Note that there are no indications in the literature that N-methylimidazole is insufficiently stable under oxidation conditions [14, 15]. We found that imidazolium and quinolinium salts are also instable under the alkane oxidation conditions. The data in Table 2 (runs 12−14) show that 4-picolinium trifluoroacetate acts approximately in the same manner as pyridinium trifluoroacetate.

Thus, the selectivity of the test systems can be controlled by introducing an ionic liquid. The effect of immobilization of a system in a high-boiling medium is also achieved in this case. This effect is of great importance in the step of catalyst separation from the products and catalyst recycle. During propane oxidation in the presence of pyridinium trifluoroacetate, a slight maximum in the acetone yield and a decrease in the ester yield are observed (Fig. 1). It can be calculated from the data of Fig. 1 that the selectivity for acetone increases from 27 to 67%.

Unfortunately, pyridinium trifluoroacetate turned out to have certain volatility, unlike N-methylimidazolinium trifluoroacetate. The vapor pressure of pyridinium trifluoroacetate steeply decreases when phosphoric acid is added. As the pyridinium trifluoroacetate concentration increases from 0 to 3 mol/L at a constant concentration of $[H_3PO_4] = 2.6$ mol/L, the
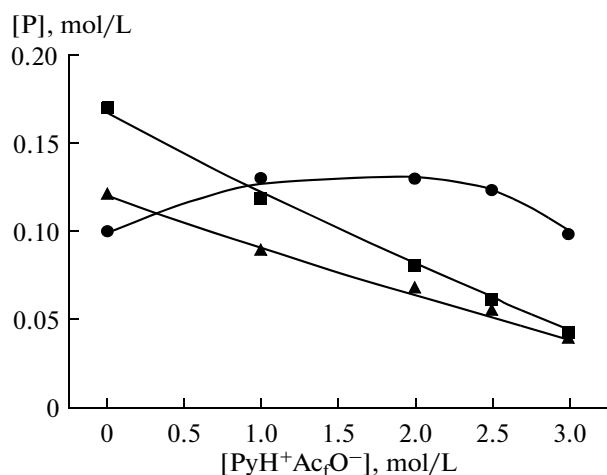
Fig. 2. The yield of propane oxidation products ([P]) versus pyridinium trifluoroacetate concentration at $[H_3PO_4]$=2.6 mol/L in the presence on the rhodium–copper–chloride catalytic system in the $CF_3COOH–H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $Cu(Ac_fO)_2 = 1 \times 10^{-1}$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L, $m_{H_2O} = 0.5$, $T = 80°C$, propane = 12.0 mmol, $O_2 = 0.8$ MPa, CO = 1.6 MPa, He = 4.0 MPa; 2.5 h: (●) acetone, (■)Ac_fOPr^i, and (▲) Ac_fOPr. Small amounts of methyl and ethyl trifluoroacetates (absent in graph) were also found.

Fig. 3. Selectivity (*S*) for total Ac_fOPr and Ac_fOPr^i and total C_3 oxygenates as a function of phosphoric acid concentration in the presence of the rhodium–copper–chloride catalytic system in the $CF_3COOH–H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $Cu(Ac_fO)_2 = 1 \times 10^{-1}$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L , propane = 12.0 mmol, $O_2 = 0.8$ MPa, CO = 1.6 MPa, He = 4.0 MPa; $T = 80°C$, $m_{H_2O} = 0.5$; 2.5 h: (●) $S_{(Ac_fOPr + Ac_fOPr^i)}$, and (■) Σ C_3 (acetone + Ac_fOPr + Ac_fOPr^i). Small amounts of methyl and ethyl trifluoroacetates (absent in graph) were also found.

acetone yield passes through a diffuse maximum and the yields of Ac_fOPr and Ac_fOPr^i decrease (Fig. 2). Thus, the patterns of the curves in this case are qualitatively similar to those in Fig. 1, but the product yields are twofold lower.

It turned the propane oxidation in the trifluoroacetic acid–water medium in the presence of phosphoric acid can be accomplished even without addition of pyridinium (picolinium) trifluoroacetate. In principle, phosphoric acid can also be classified with ionic liquids. From the data in Fig. 3, it follows that the selectivity for total Ac_fOPr and Ac_fOPr^i slightly increases and the total yield of C_3 oxygenates considerably decreases as the phosphoric acid concentration increases from 0 to 5 mol/L in the $CF_3COOH–H_2O$ medium.

In connection with this, we examined the influence of phosphoric acid on the activity of the rhodium–copper–chloride catalytic system in wider acid concentration and temperature ranges. Only traces of the products of propane oxidation in the $H_2O–H_3PO_4$ medium were observed even at 130°C in the absence of CF_3COOH (Table 4, run 1).

Further, the Ac_fOH/H_3PO_4 ratio was varied; the yields of oxygenates decreased with decreasing the ratio (Table 4, runs 2–6). Elevation of temperature resulted in the formation of a small amount of rhodium black (Table 4; runs 7, 9, 10), but the catalytic sys-
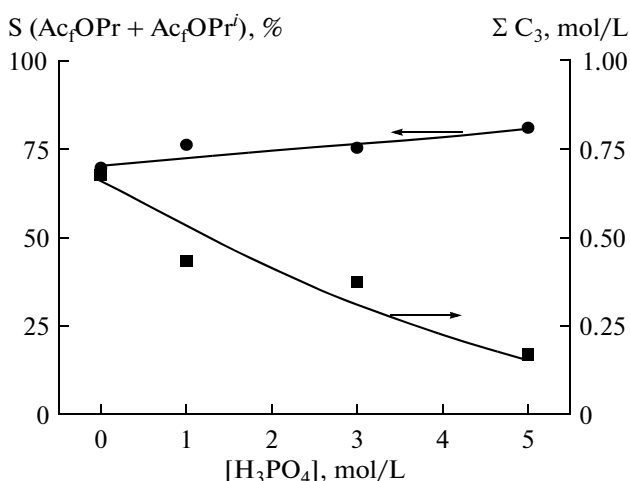
tem was stable when $[Cu(OAc_f)_2]$ was increased to 0.15–0.20 mol/L and quite acceptable yields of the propane oxidation products were obtained in runs 11 and 12 (Table 4).

Palladium compounds can be used in catalytic systems for alkane oxidation with O_2 and CO, providing that stabilizing, poorly oxidizable ligands, such as 2,2'-bipyridyl (Bipy) and 1,10-phenanthroline, are added [11]. Palladium-containing catalytic systems operate at temperatures limited to ≈85°C because of their instability with respect to CO. Table 5 lists data on propane oxidation over palladium compounds containing different anionic ligands.

The chloride complexes are the most effective. Also note that these systems do not catalyze isotope exchange with the medium. Even trace deuteromethane was not detected after a 5-h run under the following conditions: $[BipyPdCl_2] = 5 \times 10^{-3}$ mol/L, $Ac_fOD/D_2O = 2.85$ (vol), 5 mL of a solution, CH_4 pressure = 6.0 MPa (12 mmol), 95°C. Because the run was conducted in the absence of CO, the solution remained homogeneous after the reaction. It is likely that the mechanism of operation of the Pd-containing catalytic systems is close to that of the rhodium–copper–chloride system, which is also inactive in deuterium–hydrogen exchange of methane with the medium [5]. The influence of $PyH^+Ac_fO^-$ on the yield of propane oxidation products is similar to its behavior

Table 4. Effect of the trifluoroacetic acid to phosphoric acid molar ratio on the yield of propane oxidation products in the presence of the rhodium–copper–chloride catalytic system in the $CF_3COOH-H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $[Cu(Ac_fO)_2] = 1 \times 10^{-1}$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L, $m_{H_2O} = 0.5-0.58$, propane = 12 mmol, $^{16}O_2 = 0.8$ MPa, CO = 1.6 MPa, He = 4.0 MPa

No.	$Cu(Ac_fO)_2$, mol/L	Ac_fOH, mol/L	$Ac_fOH/$ H_3PO_4, mol/mol	T, °C	τ_{react}, h	Ac_fOPr^i	Ac_fOPr^n	acetone	Note
1	0.1	—	0	130	7.0	Traces	Traces	Traces	Rh black
2	0.1	9.92	9.58	80	2.5	0.19	0.14	0.095	
3	0.1	9.10	3.50	80	2.5	0.154	0.12	0.01	
4	0.1	8.48	2.34	80	2.5	0.082	0.058	0.31	
5	0.1	1.16	0.10	95	6.0	Traces	Traces	Traces	
6	0.1	1.13	0.10	110	7.0	Traces	Traces	0.04	
7	0.1	2.72	0.27	130	7.0	0.0130	0.002	0.057	Rh black
8	0.1	5.0	0.70	110	4.0	0.169	0.066	0.061	
9	0.1	5.1	0.70	120	4.0	0.24	0.060	0.10	Rh black
10	0.1	4.1	0.50	120	4.0	0.250	0.060	0.11	Rh black
11	0.15	5.12	0.70	120	2.0	0.208	0.044	0.078	
12	0.20	5.06	0.70	120	2.0	0.190	0.051	0.083	

Table 5. Propane oxidation in the presence of the Pd(II)–Bipy–Cu(II) catalytic system in the $CF_3COOH-H_2O$ medium: $[Pd(II)] = 5 \times 10^{-3}$ mol/L; Bipy = 5×10^{-3} mol/L, $[Cu(II)] = 5 \times 10^{-2}$ mol/L, $m_{H_2O} = 0.5$, $V_{solution} = 5$ mL, propane = 12 mmol, He = 4.0 MPa, $^{16}O_2 = 0.8$ MPa, CO = 1.6 MPa, 80°C, 2–3 h until approximately the same conversion of oxygen

No.	Compound	Additives	Pr^iOAc_f	$PrOAc_f$	acetone
1[a]	Na_2PdCl_4	—	0.07	0.03	0.07
2	$PdCl_2$	2NaBr	0.06	0.02	0.07
3	K_2PdBr_4	—	Traces	Traces	0.03
4	$PdBr_2$	—	0.01	Traces	0.04
5[b]	$Pd(OAc_f)_2$	—	0.03	0.02	0.06

[a] The products (over Na_2PdCl_4) also contain $MeOAc_f$, $EtOAc_f$, HCOOH, and CH_3COOH; [b] precipitation of Pd metal is observed.

Table 6. Methane oxidation in the presence the rhodium–copper–chloride catalytic system in the $CF_3COOH-H_2O$ medium: $[RhCl_3] = 5 \times 10^{-3}$ mol/L; $[Cu(Ac_fO)_2] = 0.2$ mol/L, $[NaCl] = 1.5 \times 10^{-2}$ mol/L, $CH_4 = 6.0$ MPa, CO = 1.6 MPa, $O_2 = 0.8$ MPa, $m_{H_2O} = 0.5$

No.	IL, mol/L	m_{H_2O}	T, °C	τ, h	O_2	CO	CO_2	Ac_fOMe yield, mol/L	Note
1	$[H_3PO_4] = 7.3$	0.73	120	6	1.6	10.3	15.2	0.027	Catalyzate demixes
2	$[PyH^+Ac_fO^-] = 2.1$	0.51	95	4	1.2	9.1	14.2	0.072	
3	$[PyH^+Ac_fO^-] = 2.0$ $[H_3PO_4] = 2.5$	0.51	95	4	2.2	10.4	13.3	0.05	

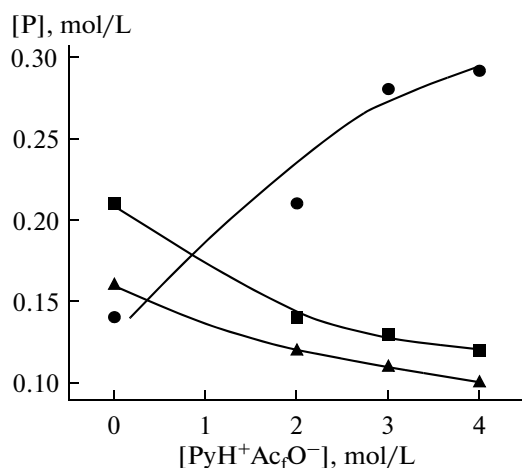(Gas phase composition, % — columns O_2, CO, CO_2)

Fig. 4. The yield of propane oxidation products ([P]) in the presence of pyridinium trifluoroacetate and the palladium–bipyridyl–copper–chloride catalytic system in the $CF_3COOH-H_2O$ medium: $[Na_2PdCl_4] = 5 \times 10^{-3}$ mol/L; [Bipy] = 5×10^{-3} mol/L, [NaCl] = 1×10^{-2} mol/L, $Cu(Ac_fO)_2 = 5 \times 10^{-2}$ mol/L, $m_{H_2O} = 0.5$, propane = 12.0 mmol, $O_2 = 0.8$ MPa, CO = 1.6 MPa, He = 4.0 MPa, 80°C; 2.5 h: (●) acetone, (■) Ac_fOPr^i, and (▲) Ac_fOPr^n. Small amounts of methyl and ethyl trifluoroacetates (absent in graph) were also found.

in the rhodium-copper–chloride catalytic system, as illustrated in Fig. 4.

With an increase in $[PyH^+Ac_fO^-]$ from 0 to 4 mol/L, the yield of acetone considerably increases and the yield of propyl esters drops by about a factor of 1.5.

Oxidation of Methane

The methane oxidation reaction occurs at higher temperatures as compared with oxidation of propane; however, the yields of methyl trifluoroacetate (Ac_fOMe) are small. For example, the yield of Ac_fOMe in the $Ac_fOH-H_2O-H_3PO_4$ medium with an almost complete exhaustion of O_2 is 0.027 mol/L even at 120°C (Table 6, run 1).

The Ac_fOMe yields in the $Ac_fOH-H_2O-PyH^+Ac_fO^-$ and $Ac_fOH-H_2O-H_3PO_4-PyH^+Ac_fO^-$ media at 95°C were 0.072 and 0.050 mol/L, respectively (Table 6, runs 2 and 3). Note that the Ac_fOMe yield in the Ac_fOH-H_2O medium under the same conditions at 95°C was 0.20−0.22 mol/L [4].

Thus, the possibility has been found to control the selectivity of the direct alkane oxidation reaction conjugated with CO oxidation by introducing an ionic liquid into the metal complex catalytic systems based on rhodium and palladium compounds and a copper salt. As a medium for immobilization of homogeneous catalysts or catalytic systems, ionic liquids and other high-boiling-point compounds can be used, a circumstance that can be important for recycling the catalyst. Acetone is produced directly from propane, not from isopropanol, regardless of the presence or absence of the IL. The pyridine- and picoline-based ILs appeared to be stable with respect to oxidative degradation; however, to reduce the volatility of pyridinium trifluoroacetate, phosphoric acid should be added. Phosphoric acid itself can be a medium for immobilization of catalytic systems, but the reaction requires higher temperatures than in the case of IL.

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