

# Homogeneous Metal-Complex Catalyst Systems in the Partial Oxidation of Propane with Oxygen

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**Abstract**—The effect of copper compounds and phosphorus–molybdenum–vanadium heteropoly acids (HPAs)  $H_5PMo_{10}V_2O_{40}$  and  $H_7PMo_8V_4O_{40}$  used as cocatalysts in the cooxidation of propane and CO in the presence of rhodium, palladium, and platinum compounds in an aqueous AcOH medium has been studied. It has been shown that these HPAs are fairly effective; however, in catalyst systems with rhodium and palladium compounds, these HPAs are inferior to Cu(I,II). The inner-sphere and outer-sphere reaction mechanisms have been studied as the most probable oxidation mechanisms; the contribution of each of the mechanisms to the overall process has been determined.

**Keywords:** alkanes, partial oxidation, carbon monoxide, rhodium, palladium, and platinum complexes, reaction mechanism, heteropoly acids

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Alkanes of natural and associated petroleum gases are an available inexpensive feedstock for the production of key oxygen-containing compounds of organic and petrochemical synthesis, namely, alcohols, aldehydes, ketones, and carboxylic acids. To date, the use of this feedstock has been limited to conversion to synthesis gas and the subsequent synthesis of methanol or hydrocarbons by the Fischer–Tropsch reaction [1, 2].

Under normal conditions, alkanes are relatively inert compounds. Conventional heterogeneous catalysts exhibiting activity at relatively high temperatures are nonselective in the direct oxidation of alkanes because of the occurrence of deep oxidation reactions [3]. Homogeneous catalysts and catalyst systems are active at lower temperatures and characterized by high selectivity [4].

The discovery of the homogeneous activation of methane by Shilov et al. [5] in 1969 has given an impetus to a rapid development of this field of chemistry. Over the past 50 years, an extensive amount of experimental and theoretical data has accumulated [6–12]; however, a catalyst appropriate for commercialization has not yet been developed.

Various compounds, such as  $H_2O_2$ ,  $K_2S_2O_8$ ,  $C_6H_5IO$ , organic peroxides, and hydroperoxides, were studied as oxidizers. It was found that the use of  $H_2O_2$  for methane oxidation to methanol is unprofitable [13]. Most probably, the commercialization of oxidation processes will require the use of molecular oxygen as a feed oxidizer, particularly, in the case of  $C_1$ – $C_4$

alkanes. In this context, oxygen activation is added to the fairly complicated stage of C–H bond activation.

To date, two main approaches to alkane activation can be distinguished. According to the first approach, alkane activation occurs in the inner coordination sphere of a catalytically active metal complex to form a metal–alkyl bond (inner-sphere mechanism (ISM)). The other mechanism consists in the use of analogies with the action of biocatalysts (oxygenases). It is assumed that, under the action of oxygenases, the C–H bond of alkanes undergoes cleavage owing to the acceptance of a hydrogen atom by the oxo (peroxo) group of the catalytically active complex. This mechanism is referred to as the outer-sphere mechanism (OSM).

Shilov systems ( $PtCl_4^{2-}$ – $PtCl_6^{2-}$ ) [4, 6, 7], Periana systems (in oleum) [7, 8], and some other systems act in accordance with the ISM. These systems are characterized by a deuterium–hydrogen isotope exchange of an alkane with a medium. In systems that act in accordance with the OSM, the isotope exchange does not occur, because a metal–alkyl bond is not formed in these systems. In the system [4, 6, 7], methane is activated by the Pt(II) aquachloride complex, while  $[PtCl_6]^{2-}$  acts as an oxidizer. The yield of products—methanol and methyl chloride—is low. In the system [8, 14, 15], the catalyst is the Pt(bipym)Cl<sub>2</sub> (bipym is bipyrimidine) complex in an oleum solution. The oxidation process occurs under the action of SO<sub>3</sub> at a

methane pressure of 3.4 MPa and 170–220°C. At a methane conversion of 90%, the yield of the product—methyl bisulfate—is 73%; however, the catalyst activity is low (8.4 h<sup>-1</sup>). This catalyst is thought of as one of the most promising catalysts.

Catalyst systems that partly or mostly act in accordance with the OSM include systems developed by us in terms of a biomimetic approach. This approach consists in the introduction of a coreducing agent. To activate molecular oxygen, biological catalysts—oxygenases—use the reduced form of nicotinamide adenine dinucleotide (NADH) as a coreducing agent. In chemical systems, it is reasonable to use hydrogen, carbon monoxide, or synthesis gas (hydrogen—carbon monoxide mixture) as coreducing agents. Later, it was found that it is necessary to introduce cocatalysts that—in the reduced form—react with molecular oxygen to convert it to active two-electron oxidizers.

Cocatalysts are compounds that readily undergo redox transitions and are commonly used as reoxidizers in the oxidation of olefins and carbon monoxide, namely, HI/HOI, Cu(I)/Cu(II), and Fe(II)/Fe(III). Using this approach, a number of homogeneous catalyst systems for the oxidation and oxidative carbonylation of methane and other lower alkanes have been developed [9–12]. For example, in the presence of a rhodium—copper—chloride catalyst system in an aqueous trifluoroacetic acid (Ac<sub>f</sub>OH) medium at 6 MPa and 95°C, methane is converted to organic oxygenates (methanol, formic and acetic acids) at a total activity of 100–150 h<sup>-1</sup> in terms of Rh.

It appeared important to expand the range of cocatalysts and involve heteropoly acids (HPAs) in the design of catalyst systems. These compounds are attractive owing to their diversity; they have been commonly used as catalysts for the oxidation of various organic substrates [16, 17] and as reoxidizers in the composition of catalyst systems for the oxidation of CO and olefins [18–21]. It was reported that an HPA acts as a cocatalyst in the oxidation of C<sub>3</sub>–C<sub>4</sub> alkanes in the presence of Ru(IV) complexes in an aqueous medium [22] and methane oxidation in the presence of a SiO<sub>2</sub>-supported Pt(bipym)Cl<sub>2</sub> complex [23]. In this case, in the presence of Ru(IV) complexes, the main product—acetone—is formed from propane with a yield that is significantly lower than the stoichiometric yield. In the presence of a Pt(bipym)Cl<sub>2</sub>/SiO<sub>2</sub> catalyst, methane is converted not only to methanol, but also to acetaldehyde. In addition, it was reported that H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> was used as a cocatalyst in systems with Pd(OAc)<sub>2</sub> and Pd(bipy)Cl<sub>2</sub> in an Ac<sub>f</sub>OH medium [24, 25]. The H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> compound is insoluble in Ac<sub>f</sub>OH; apparently, this cocatalyst exhibits activity in the form of a suspension. It is significant that HPAs act as a binding agent between a support and a catalytically active complex [26]. This factor opens up the prospects for synthesizing heterogenized catalysts in which an HPA can simultaneously act as a binder and

a cocatalyst. However, before the synthesis, it is necessary to study HPAs as cocatalysts under conditions of homogeneous catalysis.

The aim of this study is to explore the possibility of using HPAs as cocatalysts and compare their efficiency with that of Cu(II) in propane oxidation in an aqueous acetic acid medium in the presence of rhodium, palladium, and platinum compounds under the action of an O<sub>2</sub>–CO mixture.

## EXPERIMENTAL

### *Materials and Reactants*

In this study, RhCl<sub>3</sub> · (H<sub>2</sub>O)<sub>x</sub> (34 wt % Rh), K<sub>2</sub>PdCl<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> were synthesized as described in [27]; NaCl (reagent grade), Cu(OAc)<sub>2</sub> · H<sub>2</sub>O (analytical grade), CuSO<sub>4</sub> · 5H<sub>2</sub>O (reagent grade), CH<sub>3</sub>COOH (reagent grade), H<sub>2</sub>SO<sub>4</sub> (reagent grade), perfluorooctanesulfonic acid (PFOSA, a 40% solution in water, Sigma-Aldrich), α,α-bipyridyl, γ,γ-bipyridyl (Sigma-Aldrich), and H<sub>2</sub>O (bidistillate) were used. Esters of acetic acid and alcohols (propanols, *n*-butanol) were synthesized as described in [28] and distilled. The purity of the esters was controlled by gas chromatography (GC). Propanal (99.5%, Sigma-Aldrich) HPA was synthesized according to [29]. The following gases were used: CO (99.9%), C<sub>3</sub>H<sub>8</sub> (99.8%), O<sub>2</sub> (99.9%), electrolytic H<sub>2</sub>, and grade A helium.

### *Catalytic Testing Procedure*

Tests were conducted in a 34-cm<sup>3</sup> thermostatically controlled fluoroplastic-lined stainless steel reactor. The contact solution (liquid phase volume of 2.5 mL) was prepared in a special container. To provide accurate dosing, the catalyst system components were weighed on an analytical balance; after that, the mass from the container was loaded into the reactor. The reactor was connected to a gas supply unit; C<sub>3</sub>H<sub>8</sub>, O<sub>2</sub>, and CO gases were sequentially fed to a partial pressure of 0.68, 0.4, and 0.88 MPa, respectively. A 10-MPa standard pressure gage with a division value of 0.04 MPa was mounted in the gas supply line to provide an accurate dosing of gases. Once the gases were fed, the reactor valve was closed; the reactor was connected to a thermostat preheated to the test temperature, and stirring was switched on. After the test, the reactor was cooled with running water to room temperature.

### *Analysis Procedures*

The gas and liquid phases were analyzed by GC. The gas phase was analyzed on an LKhM-2000 chromatograph with the Z-Lab software at 55°C using a thermal conductivity detector. The following columns were used: 5-Å molecular sieves with a grain size of

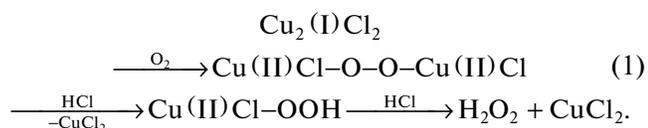
0.2–0.3 mm,  $l = 3$  m,  $d = 3$  mm, and He = 30 mL/min ( $O_2$ ,  $N_2$ ,  $CH_4$ , CO) and a Porapak Q with a grain size of 0.115–0.200 mm,  $l = 2$  m,  $d = 2.5$  mm, and He = 20 mL/min ( $CO_2$ , propane).

The liquid phase was analyzed on a Kristallyuks 4000M gas chromatograph using the NetChrom V2.1 software, an Agilent CP-Sil-5CB capillary column with  $l = 25$  m and  $d = 0.15$  mm, temperature programming of 40–150°C at a rate of 5 deg/min, He = 20 mL/min, a column inlet pressure of 1.3 atm, a split ratio of 1 : 70, and a flow rate of 0.287 mL/min. The samples were injected into the chromatograph evaporator after preconditioning.

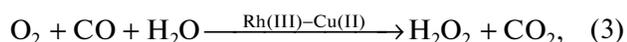
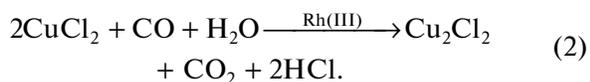
**Preconditioning procedure for GC analysis.** A catalyzate with the introduced internal standard ( $n-C_4H_9OAc$ ) was loaded into a special reactor with a chromatographic silicone membrane subjected to thermostating at 50°C for 10 min. After that, a gas-vapor sample was taken using a gas syringe heated to 60°C. The amount of the sample introduced into the chromatograph was 100–150  $\mu$ L.

## RESULTS AND DISCUSSION

The efficiency of copper compounds as cocatalysts in the homogeneous oxidation of alkanes in the presence of rhodium and palladium complexes was revealed earlier for media containing a mixture of water and  $Ac_fOH$  [30, 31] or heptafluorobutyric acid ( $Pr_fCOOH$ ) [32]. The action of copper compounds is attributed to the specificity of the reaction between Cu(I) and oxygen, which, under certain conditions, is accompanied by the formation of significant amounts of hydrogen peroxide [33] according to the sequence of reactions (1):

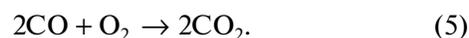
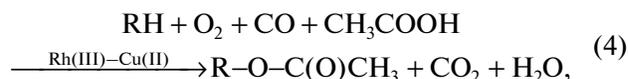


In this case, not only hydrogen peroxide, but also copper(II) peroxides and hydroperoxides can be active two-electron alkane oxidizers. In the case of a continuous reduction of Cu(II) to Cu(I) (reaction (2)), the formation of two-electron oxidizers becomes a catalytic process (reaction (3)):



The developed catalyst systems exhibit activity upon the introduction of CO as a coreducing agent. There are reports on catalyst systems exhibiting activity without the introduction of a coreducing agent [24, 25, 34–36]. However, the activity of these systems is extremely low even in an  $Ac_fOH$  medium.

Since HPAs are hardly soluble in  $Ac_fOH$ , the possibility of using them as cocatalysts for propane oxidation was studied in aqueous  $AcOH$ . Water is an important component of catalyst systems for the cooxidation of alkanes and CO (reactions (2) and (3)). Taking into account the poor water solubility of propane, previous studies showed that the water content should be maintained at an optimum level of ~20 vol %. The cooxidation of alkane and CO is described by Eq. (4). Simultaneously, intense CO oxidation occurs (reaction (5)).



### Catalyst Systems Based on Rhodium Complexes

A comparative study of the  $RhCl_3-Cu(II)-NaCl$ ,  $RhCl_3-H_5PMo_{10}V_2O_{40}$  (HPA-2), and  $RhCl_3-H_7PMo_8V_4O_{40}$  (HPA-4) catalyst systems was conducted. Typically, copper compounds are active as reoxidizers in fairly acidic media. In the absence of  $H_2SO_4$ , only carbonyl compounds were identified in the reaction products; the dominant product was propanal (Table 1, test 1). Note that, to provide an activity of a rhodium–copper–chloride catalyst system, it is necessary to introduce excess  $Cl^-$ , because Cu(II) acts as a cocatalyst (reoxidizer) in the presence of  $Cl^-$  in the coordination sphere of it [37]. In the absence of excess  $Cl^-$ , moderate catalytic activity is observed (Table 1, test 2). The introduction of  $H_2SO_4$  into the  $RhCl_3-Cu(OAc)_2$  system also contributes to a more correct comparison with Rh–HPA catalysts (HPAs are strong acids). The addition of  $H_2SO_4$  leads to a significant increase in catalytic activity (Table 1, tests 3, 4). At a sulfuric acid concentration of 0.05 and 0.1 M, the catalytic activity is almost identical (Table 1, tests 3, 4). A number of tests were conducted in the presence of  $RhCl_3-NaCl-\alpha,\alpha$ -bipy( $\gamma$ - $\gamma$ -bipy)- $Cu(OAc)_2$  catalyst systems. The introduction of bipy ligands is necessitated by the following. A study of the properties of the  $RhCl_3-Cu(OAc)_2$  catalyst system heterogenized on  $\gamma-Al_2O_3$  in the CO oxidation reaction in a gas-flow unit revealed a partial of rhodium in the form of  $Rh_2Cl_2(CO)_4$  from the catalyst [38]. It was assumed that the introduction of bipy ligands will lead to an abrupt decrease in the volatility of rhodium carbonyls. Tests 5 and 6 conducted at  $T = 90^\circ C$  (Table 1) show that  $\alpha,\alpha$ -bipy leads to a significant decrease in the activity of the catalyst system; this fact is apparently attributed to the formation of stable chelate complexes. The introduction of  $\gamma,\gamma$ -bipy has hardly any effect on the catalytic activity (Table 1, test 7).

Data on the study of HPAs as cocatalysts are shown in Table 1 (tests 9–14). The catalyst systems with HPA-4 exhibit low activity (Table 1, tests 9–11). It was

**Table 1.** Reaction product composition, catalytic activity, and contribution of the ISM in the cooxidation of propane and carbon monoxide in the presence of RhCl<sub>3</sub> and cocatalysts\*

No.	[RhCl <sub>3</sub> ] × 10 <sup>3</sup> , M	Additives		[Cocatalyst], M	τ, h	Products				A, h <sup>-1</sup>	S, vol %
		[NaCl] × 10 <sup>3</sup> , M	[H <sub>2</sub> SO <sub>4</sub> ], M			CO <sub>2</sub> , vol %	oxygenates from propane, M × 10 <sup>3</sup>				
							<i>i</i> -PrOAc	<i>n</i> -PrOAc	∑ C <sub>3</sub> H <sub>6</sub> O (Pa : Ac)		
1	2.5	7.5	0	Cu(OAc) <sub>2</sub> , 0.02	2	19.9	Traces	Traces	0.015 (64 : 36)	3	64
2	2.5	0	0.05	Cu(OAc) <sub>2</sub> , 0.02	2	16.3	29	22	22	14.6	—
3	2.5	7.5	0.05	Cu(OAc) <sub>2</sub> , 0.02	2	8.2	75	51	45 (23 : 77)	34	47
4	2.5	7.5	0.1	Cu(OAc) <sub>2</sub> , 0.02	1.7	8.2	86	47	47 (27 : 73)	36	42
5	2.5	7.5	0.11	Cu(OAc) <sub>2</sub> , 0.02	2	2.77	14	6	31	10	—
α,α-bipy											
6	2.5	1.5	0.1	CuSO <sub>4</sub> · 5H <sub>2</sub> O, 0.02	2.5	5.1	33	16	49	16	—
α,α-bipy											
7	2.5	7.5	0.1	CuSO <sub>4</sub> · 5H <sub>2</sub> O, 0.02	2	8.3	83	44	47 (20 : 80)	35	39
γ,γ-bipy											
8	2.5	7.5	0.1	CuSO <sub>4</sub> · 5H <sub>2</sub> O, 0.02	2	18.8	90	43	61	39	—
9	5	15	0	HPA-4, 0.02	2	1.6	4	0	12	3.2	—
10	2.5	0	0	HPA-4, 0.02	2	16.3	4	Traces	13	3.4	—
11	2.5	0	0.05	HPA-4, 0.02	2	5.7	3	0	7	2.0	—
12	5	15	0	HPA-2, 0.02	2	4.4	0.5	1	32	3.8	—
13	2.5	0	0.05	HPA-2, 0.02	3	8.9	13	7	14	13.6	—
14	2.5	0	0	HPA-2, 0.02	1	29.4	8	8	42 (50 : 50)	23	55
15	2.5	7.5	0	PFOSA, 0.1; Cu(OAc) <sub>2</sub> , 0.02	2	24.4	83.61	35.4	27.9	29.4	—
16	2.5	0	0	PFOSA, 0.1; HPA-2, 0.02	2	7.19	19.34	6.7	14.8	8.2	—

\* Test conditions: gas pressure at room temperature: C<sub>3</sub>H<sub>8</sub>, 6.8; O<sub>2</sub>, 4.0; and CO, 8.8 atm; AcOH : H<sub>2</sub>O = 4 : 1 (vol/vol); 80°C; in tests 5 and 6, 2.5 × 10<sup>-3</sup> M [α,α-bipy] is introduced; in test 7, 2.5 × 10<sup>-3</sup> M [γ,γ-bipy] is introduced; in tests 5 and 6, T = 90°C; ∑ C<sub>3</sub>H<sub>6</sub>O is the sum of propanal and acetone; Pa : Ac is the propanal to acetone molar ratio; A is the activity of the catalyst system expressed in terms of turnover frequency, h<sup>-1</sup>; and S is the contribution of the ISM.

**Table 2.** Reaction product composition, catalytic activity, and contribution of the ISM in the cooxidation of propane and CO in the presence of Pd-containing catalyst systems,  $[K_2PdCl_4] = [\alpha, \alpha\text{-bipy}] = 2.5 \times 10^{-3} \text{ M}^*$ 

No.	[Cocatalyst], M	$[H_2SO_4]$ , M	$\tau$ , h	Products			$A$ , $h^{-1}$	$S$ , mol %	
				$CO_2$ , %	oxygenates from propane, $M \times 10^3$				
					<i>i</i> -PrOAc	<i>n</i> -PrOAc			$\sum C_3H_6O$ (Pa : Ac)
1	$Cu(OAc)_2$ , 0.04	0	1.0	6.5	Traces	Traces	23.5 (56 : 44)	9.4	56
2	$Cu(OAc)_2$ , 0.04	0.05	1.5	8.0	20.2	23.3	45.0 (31 : 69)	35.4	51
3	$Cu(OAc)_2$ , 0.04 HPA-2, 0.02	0	1.0	13.4	7.2	Traces	23.0	12.0	
4	$Cu(OAc)_2$ , 0.04 HPA-4, 0.02	0	1.0	14.4	8.3	1.6	19.5	11.8	
5	$Cu(OAc)_2$ , 0.04 HPA-2, 0.02	0.05	1.0	33.0	9.9	4.9	14.8	11.8	
6	HPA-4, 0.02	0	1.0	12.3	10.2	2.9	18.1 (57 : 43)	12.4	45
7	HPA-2, 0.02	0	1.0	32.5	5.8	4.7	39.3 (50 : 50)	19.9	52
8	HPA-4, 0.02	0.05	1.0	12.1	11.2	3.3	26.8	16.5	
9	HPA-2, 0.02	0.05	1.0	37.4	26.5	13.5	19 (63 : 37)	23.6	51

\* Test conditions: gas pressure at room temperature:  $C_3H_8$ , 6.8;  $O_2$ , 4.0; and  $CO$ , 8.8 atm;  $AcOH : H_2O = 4 : 1$  (vol/vol);  $80^\circ C$ ;  $\sum C_3H_6O$  is the sum of propanal and acetone; Pa : Ac is the propanal to acetone molar ratio;  $A$  is the activity of the catalyst system expressed in terms of turnover frequency,  $h^{-1}$ ; and  $S$  is the contribution of the ISM.

found that excess  $Cl^-$  inhibits the activity of HPA-2 as cocatalysts for the oxidation of propane and carbon monoxide (Table 1, tests 12, 14). The inhibition can be associated with the formation of V(IV) chloride compounds, which already cannot be part of HPAs and undergo reoxidation with oxygen.

Catalyst systems based on HPAs as reoxidizers instead of Cu(II) were developed as chloride-free systems to decrease the corrosion severity of contact solutions during ethylene oxidation to acetaldehyde [20]. The  $RhCl_3$ -HPA-2 catalyst system exhibited a quite acceptable activity, although it was slightly lower than that of the  $RhCl_3$ - $Cu(OAc)_2$ -NaCl system (Table 1, test 14). The low efficiency of HPA-4 can be attributed to the fact that it has a lower oxidation potential than that of HPA-2 [21]. Upon the addition of  $H_2SO_4$  to a  $Cu(OAc)_2$  solution, it is reasonable to expect the presence of  $Cu^{2+}$ ,  $OAc^-$ , and  $SO_4^{2-}$  in the solution. Therefore,  $CuSO_4$  was used as a cocatalyst in tests 6–8 (Table 1). However, comparison of tests 4 and 8 (Table 1) shows that there is hardly any difference between these cocatalysts. To synthesize heterogenized catalysts, the most appropriate acidic additive is a strong organic acid, such as PFOSA, rather than  $H_2SO_4$ . Therefore, the tests were conducted in the presence of  $Cu(OAc)_2$  or HPA-2 as cocatalysts; the test results were quite acceptable (Table 1, tests 15, 16).

#### Catalyst Systems Based on Palladium Complexes

In all the tests, an  $\alpha, \alpha$ -bipy stabilizing ligand was added to prevent the precipitation of metallic palladium. In the case of using  $Cu(OAc)_2$  as a cocatalyst, esters (*i*-PrOAc and *n*-PrOAc) were detected in trace amounts; the main reaction products were  $\sum C_3H_6O$  (sum of propanal and acetone) (Table 2, test 1). Apparently, in this case, a significant contribution comes from the OSM, and acetone is formed directly from propane, rather than through the intermediate isopropanol. This mechanism was proposed earlier in the case of cooxidation of propane and  $^iPr^{18}OH$  with oxygen  $^{16}O_2$ . In that case, the only reaction product was  $CH_3-(^{16}O)C-CH_3$  [39]. Upon the acidification of the contact solution with sulfuric acid, significant amounts of esters were detected; however, the yield of  $\sum C_3H_6O$  also increased (Table 2, test 2). The introduction of HPA-2 and HPA-4 as an acidic promoter led to a decrease in catalytic activity (Table 2, tests 3, 4). The addition of  $H_2SO_4$  did not affect the catalytic activity (Table 2, test 5). The use of HPA-4 and HPA-2 provides a moderate catalytic activity (Table 2, tests 6, 7), whereas acidification with sulfuric acid leads to a considerable increase in catalytic activity (Table 2, tests 8, 9).

Thus, catalyst systems based on Pd complexes and HPAs exhibit a significant catalytic activity in the partial oxidation of propane; however, as in the case of systems based on Rh complexes, the activity is still

**Table 3.** Reaction product composition, catalytic activity, and contribution of the ISM in the cooxidation of propane and CO in the presence of platinum complexes and cocatalysts\*

No.	[Cocatalyst], M	[H <sub>2</sub> SO <sub>4</sub> ], M	$\tau$ , h	Products			$A$ , h <sup>-1</sup>	$S$ , mol %	
				CO <sub>2</sub> , %	oxygenates from propane, M × 10 <sup>3</sup>				
					<i>i</i> -PrOAc	<i>n</i> -PrOAc			$\sum$ C <sub>3</sub> H <sub>6</sub> O (Pa : Ac)
1	Cu(OAc) <sub>2</sub> , 0.02	0.04	1.7	2.0	Traces	Traces	Traces	0	—
2	Cu(OAc) <sub>2</sub> , 0.04*	0.05	1.7	8.2	11.3	12.6	7.6	3.7	—
3	HPA-2, 0.04	0	2.0	11.2	23.7	5.6	45.7 (47 : 53)	7.6	38
4	HPA-2, 0.04	0.05	1	27.5	21.9	11.2	52.7 (64 : 36)	17	57

\* Test conditions: gas pressure at room temperature: C<sub>3</sub>H<sub>8</sub>, 6.8; O<sub>2</sub>, 4.0; and CO, 8.8 atm; AcOH : H<sub>2</sub>O = 4 : 1 (vol/vol); 80°C; (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> = 5 × 10<sup>-3</sup> M; in test 2,  $\sum$  Cl/Pt = 12, [(NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>] = 5 × 10<sup>-3</sup> M, [NaCl] = 3 × 10<sup>-2</sup> M;  $\sum$  C<sub>3</sub>H<sub>6</sub>O is the sum of propanal and acetone; Pa : Ac is the propanal to acetone molar ratio;  $A$  is the activity of the catalyst system expressed in terms of turnover frequency, h<sup>-1</sup>; and  $S$  is the contribution of the ISM.

lower than that of systems containing Cu(OAc)<sub>2</sub> as a cocatalyst. Apparently, the reoxidation of reduced HPA forms with oxygen occurs more slowly than the oxidation of Cu(I) to Cu(II). The use of HPA-4, as in the case of rhodium-containing systems, is less efficient than the use of HPA-2. However, HPAs have a certain advantage over Cu(II); that is, they do not form insoluble precipitates during reduction. In addition, according to the authors of [18, 20], HPAs stabilize Pd(0) to some extent and prevent the precipitation of Pd in the form of a metallic precipitate.

#### Catalyst Systems Based on Platinum Complexes

These systems were synthesized using (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> as the precursor. Under the test conditions (CO, 80°C), Pt(IV) is reduced to Pt(II). Platinum compounds have an advantage over palladium compounds in reactions involving CO: the resulting Pt(0) carbonyls are significantly more stable than Pd carbonyls and the probability of precipitation of metallic platinum is low [34, 35]. In the case of using Cu(OAc)<sub>2</sub> as the cocatalyst, only traces of propane oxidation products are detected (Table 3, test 1). Upon the introduction of an additional amount of chlorine ions, the system exhibits a slight catalytic activity (Table 3, test 2). At the same time, HPA-2 provides a significant catalytic activity, which considerably increases upon the addition of sulfuric acid to the system (Table 3, tests 3, 4).

#### To the Process Mechanism

The action of HPAs as a cocatalyst is apparently similar to the action of Cu(I) and Cu(II) in copper-containing cocatalysts (reaction (1)). The reduced form of HPA contains V<sup>4+</sup>, which reacts with oxygen to undergo oxidation to form active two-electron oxidizers.

In the homogeneous oxidation of alkanes catalyzed with metal complexes in accordance with the ISM, primary alcohols are dominant in the reaction products. In propane, the energy of the primary C—H bond (in the methyl group) is 406 kJ/mol; the energy of the secondary C—H bond (in the methylene group) is 393 kJ/mol. For steric reasons, the localization of a normal alkyl in the inner coordination sphere of a metal is more advantageous than the localization of a branched alkyl. Therefore, during propane oxidation, in the [PtCl<sub>4</sub>]<sup>2-</sup>—[PtCl<sub>6</sub>]<sup>2-</sup> system, which acts exclusively in accordance with the ISM, the ratio of *n*-propyl chloride (*n*-propanol) to isopropyl chloride (isopropanol) is 3 : 1 [4, 6].

In accordance with the OSM, an alkane is activated owing to the abstraction of a hydrogen atom from the alkane by an oxygen atom of the metal oxo or peroxo complex. Since the secondary C—H bond is less strong, it is mostly this bond that undergoes oxidation. For example, in propane oxidation in the cytochrome P450—NADPH—O<sub>2</sub> biomimetic system, the only reaction product is isopropanol [42].

Earlier, it has been shown that methane oxidation in the presence of a rhodium—copper chloride catalyst system in an Ac<sub>r</sub>OH—H<sub>2</sub>O medium occurs mostly in accordance with the OSM [43]. Under the same conditions, propane oxidation partly occurs in accordance with the ISM; however, the quantitative contribution of this mechanism has not been determined [32].

In this study, the propanal to acetone ratio was given for some tests.

Let us assume, according to [5], that 25% of isopropanol are formed in accordance with the ISM, while the remaining 75% are formed in accordance with the OSM. According to [39], acetone is formed in an independent reaction, rather than in isopropanol oxidation. This independent reaction most probably occurs in accordance with the OSM. Propanal can

readily be formed in *n*-propanol oxidation. In this case, the origin of propanal is associated with the route in accordance with the ISM. Taking into account the above, it is possible to approximately determine the contribution of each of the mechanisms to the formation of the propane oxidation reaction products.

These calculations show that, in all the tests, the contribution of the ISM is extremely significant (Tables 1–3, *S* is the contribution of the ISM). In a number of tests, isopropanol and acetone dominate over *n*-propanol and *n*-propanal. In this case, the total activity of the catalyst systems is fairly high; the contribution of the ISM is lower than that of the OSM (Table 1, tests 3, 4, 7). In the RhCl<sub>3</sub>–HPA-2 catalyst system, the C<sub>3</sub>H<sub>6</sub>O yield exceeds the ester yields; the propanal and acetone yields are identical. The contribution of the ISM is 55% (Table 1, test 14). In the Pd-containing catalyst systems with both Cu(OAc)<sub>2</sub> and HPA-2, the contributions of the OSM and ISM are approximately identical (Table 2, tests 1, 2, 7, 9). In the Pt-containing catalyst systems, the best results were obtained in the case of using HPA-2 as the cocatalyst; the addition of H<sub>2</sub>SO<sub>4</sub> led to an increase in the activity and the contribution of the ISM from 38 to 57% (Table 3, tests 3, 4).

The derived data show that, by varying catalysts and cocatalysts, the process selectivity can be controlled, to a certain extent, to produce mostly alcohols (esters) or carbonyl compounds (propanal, acetone).

Disadvantages of homogeneous liquid-phase catalysis are the complexity of separating the catalyst from the reaction products and the solvent and returning the catalyst to the catalytic process and the high corrosion severity of the used media. In this context, it appears promising to design hybrid homogeneous–heterogeneous catalysts—supported homogeneous catalysts in a high-boiling solvent—that can be used in a conventional gas-flow reactor. To make these systems active, it is necessary to provide the possibility of reaction between the catalyst system components. In this respect, HPAs can have an advantage over Cu(I,II), because they do not form insoluble compounds. Earlier, it has been found that rhodium–copper–chloride and palladium–copper–chloride catalyst systems immobilized on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are effective in the gas-phase oxidation of CO [38, 44]; however, in this case, it is necessary to introduce an acidic promoter and water vapors. However, it was impossible to simulate conditions for the cooxidation of propane and CO in the presence of these catalysts. Using the results of this study, it is possible to expand the range of cocatalysts and acidic promoters, for example, by the inclusion of H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> and perfluorosulfonic acids, and make an attempt to implement the cooxidation of propane and CO to produce oxygenates (propanols, acetone, propanal) from propane under heterogeneous catalysis conditions.

## CONCLUSIONS

(i) Thus, a comparative study of the catalytic activity of systems based on rhodium, palladium, and platinum compounds in propane oxidation in an aqueous acetic acid medium using copper compounds or phosphorus–molybdenum–vanadium HPAs as cocatalysts has been conducted. It has been shown that the systems exhibit catalytic activity only upon the introduction of CO as a reducing agent; upon switching from Cu(II) compounds to HPAs, the activity increases for the Pt catalysts and decreases for the Rh and Pd systems. The contribution of the ISM and OSM to the activation and oxidation of propane has been determined; it has been found that the role of HPAs in propane oxidation is similar to that of copper compounds.

(ii) The use of HPAs as cocatalysts is promising for designing heterogenized catalyst systems based on inorganic or polymeric porous supports.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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