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Catalytic Oxidation of Hydrocarbons of Natural and Oil Gas

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Abstract—Alkane oxidation by O_2 and CO in the presence of Rh-, Pd-, and Pt-containing catalytic systems leads to the product of C–H bond oxidation and the products of C–C bond oxidative destruction. A deuterated methyl group in acetic acid is observed in the oxidation of *n*-propane in a deuterium-donor medium. The possible mechanisms of alkane C_2–C_4 conversion are proposed.

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INTRODUCTION

The development of one-stage methods for the synthesis of the main oxygenates from natural and oil gas is an important task of petroleum chemistry. The C–H bond activation and functionalization in saturated hydrocarbons under mild conditions in the presence of metal complexes has been discussed in [1–6]. The participation of metal complexes in the cleavage of the C–C bond has also been reported [7–9]. Because of the high temperatures, conventional heterogeneous catalysis does not allow alkanes to be selectively oxidized into high-tech products [10]. It is promising to consider the activation of saturated hydrocarbons analogous to biocatalytic ones [11]. For such systems, a reducing agent should be present together with an oxidant. The oxidation of this agent generates active intermediates that are capable of selectively oxidizing alkanes. Thus, systems consisting of rhodium chloride and cocatalysts—compounds of iodine, copper (or iron), and alkali metal chlorides—are active in the coupled oxidation of methane and carbon monoxide by molecular oxygen in an aqueous solution of trifluoroacetic acid [12–16].

Carbon monoxide oxidation by oxygen in the catalytic system of platinum metal salt–halogenide can be described by the following reactions:

$$M^n + CO + H_2O \longrightarrow M^{n-2} + CO_2 + 2H^+, \quad (1)$$

$$Mn^{-2} + 2Cu(II) + 2H^+ \longrightarrow M^n + 2Cu(I), \quad (2)$$

$$2Cu(I) + 2H^+ + ½O_2 \longrightarrow 2Cu(II) + H_2O, \quad (3)$$

$$2Cu(I) + 2H^+ + O_2 \longrightarrow 2Cu(II) + H_2O_2. \quad (4)$$

In these reactions, the intermediate formation of hydrogen peroxide and other peroxo derivatives of rhodium in the high oxidation states is possible, which presumably oxidize methane [17].

The goal of this work is to elucidate the main aspects of the mechanism of the catalytic oxidation of C_2–C_4 alkanes in the presence of Rh-, Pt-, and Pd-containing catalytic systems.

EXPERIMENTAL

The following reagents were used in this work: $RhCl_3 \cdot (H_2O)_n$ (34.5 wt % Rh), $PdCl_2$ (59.5%), $PdBr_2$ (39.6%), K_2PdBr_4 (21.0%), NaCl, CuO (chemically pure), CF_3COOH (chemically pure), D_2O (99.9%), CF_3COOD (99.9%), and double-distilled H_2O. Gases: helium (grade A), N_2 (special purity grade), CO (99.9%), O_2 (99.5%), methane (99.8%), ethane (99.5%), propane (99.2%), butane (99.9%), and isobutane (99.5%). Under experimental conditions, CuO was rapidly dissolved in the reaction mixture to form trifluoroacetate. Catalytic experiments were carried out in a constant-temperature shaken stainless steel reactor lined with fluoroplastics.

In a typical run of methane oxidation, a reactor was charged with 10.0 mg CuO and a 2.5-ml solution prepared by mixing 0.5 ml of an aqueous solution of $RhCl_3$ (0.05 M) and NaCl (0.15 M), 1.4 ml H_2O, and 8.1 ml CF_3COOH. To maintain the accuracy of the concentration, the contact solution was prepared by weighing all components, including the liquids, in a special container. The reactor was sealed and attached to the unit for gas mixing equipped by a standard pressure gage (with a maximum of 10 MPa and a division value of 0.04 MPa). The following gases were supplied: CH_4 (6.00 MPa), O_2 (0.56 MPa), and CO (1.84 MPa). The autoclave jacket was attached to an ultrathermostat preliminarily heated to 80°C. Experiments were carried out for 2 h under conditions of intense stirring using a shaker. After each run, the reactor was cooled to 10–12°C, the gas was discharged into an evacuated vessel, and its composition was analyzed by gas chromatography. The gas composition (mol %) was CH_4 = 66.1, CO = 11.8, O_2 = 3.0, and CO_2 = 8.7. To analyze the liquid phase, 1.0 ml was withdrawn and 20 μl of dioxane was added as an internal GC standard. The composition of the liquid phase was as follows (M): CF_3COOCH_3 = 0.1, HCOOH = 0.04, and CH_3COOH = 0.03. Experiments on C_2–C_4 alkane oxidation were carried out in an analogous way, but alkanes (12 mmol) were initially condensed from a calibrated gas burette in an intermediate metering device and then added to the reactor under helium pressure. Helium was also introduced to prevent the formation of explosive mixtures and to make the analysis of the gas phase more convenient. Then, O_2 (0.56 MPa) and CO were supplied to the reactor. Alcohols were oxidized under the same conditions as alkanes. Under reaction conditions, alcohols converted into the thrifluoroacetatic acid esters to an extent of 90%. After the runs, the reactor was cooled to 10–12°C. The gas was collected in an evacuated vessel and its composition was analyzed by gas chromatography using a Model 3700 chromatograph with zeolite 5A (2 m × 3 mm) and Porapak Q (2 m × 3 mm) columns. The quantitative and qualitative analyses of the alkane oxidation products were carried by ^{1}H NMR with an external standard (DMSO in D_2O, capillary) using A-C200 P, Bruker 200 MHz, and BC 587 A Tesla 80 MHz instruments; by gas chromatography (Kristallyuks 4000M, columns Separon CHN and Separon SDA 2 m × 3 mm 0.125–200 mm); and by gas chtomatography coupled with mass spectrometry (Automass 150, column CP-Sil 5 0.15 mm × 25 m × 1.2 μm). Isotope-substituted products were detected using the mass spectrum averaged by the chromatographic peak of acetic acid (*m/z* 44, 45, 46, Fig. 1), methyl trifluoroacetate, and ethyl trifluoroacetate.

RESULTS AND DISCUSSION

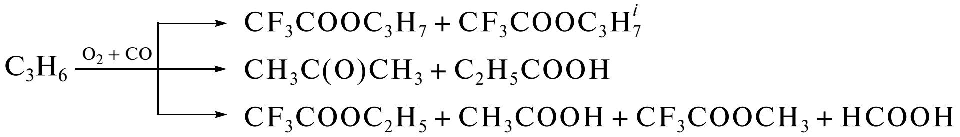
In the oxidative functionalization of C_1–C_4 alkanes under the action of O_2 and CO, catalytic systems were studied that contained Rh, Pd, and Pt halides and Cu compounds. In aqueous trifluoroacetic acid, methane is converted according to the following equations (Table 1):

$$CH_4 + CO + O_2 \longrightarrow CH_3OH\,(CF_3COOCH_3) + CO_2, \quad (5)$$

$$CH_4 + CO + O_2 \longrightarrow CH_3COOH + CO_2, \quad (6)$$

$$CH_4 + 2CO + 5/2O_2 \longrightarrow HCOOH + 2CO_2 + H_2O. \quad (7)$$

The oxidation of C_2–C_4 alkanes affects both C–H and C–C bonds as illustrated in Scheme 1 using an example of propane.

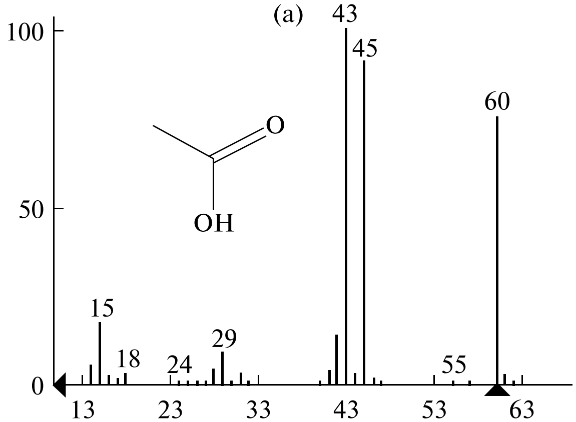


Scheme 1.

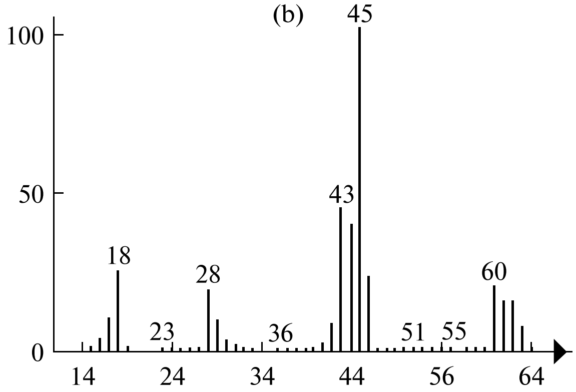
In the catalytic system containing Pd and Pt chlorides, to prevent the formation of metal blacks, ligands such as α,α-bipyridyl (bipy), 1,10-phenathroline (phen) that are hard to oxidize were introduced into the system. These ligands help to preserve the low-valence compounds of Pd and Pt in the solution. Palladium-containing systems were stable at <85°C, and platinum-containing systems partially underwent the reductive destruction to metallic platinum. The catalytic activities of the Pd(II)–bipy and Pd(II)–phen systems were approximately the same (Table 1).

Under reaction conditions, the product of methane oxidation, methanol, is converted into formic acid, which is rather stable and is accumulated in the reaction solutions. The rate of methyl trifluoroacetate oxidation is much lower, and esterification, therefore, prevents methanol from further oxidation to a large degree. Furthermore, in the absence of alkanes, HCOOH and Ac_fOCH_3 were not found. Therefore, one may assume that they are not the products of alkane oxidation.

The qualitative composition of the alkane oxidation products in all of the catalytic systems studied is the same, but the yield is higher in the presence of Rh(III) compounds. Therefore, here we will only consider the catalytic system $RhCl_3/Cu(II)/Cl^-$. The ratio between the products of alkane oxidation with and without oxidative destruction depends on the length of a chain and on the degree of alkane branching. Thus, in ethane oxidation (Table 2), the hydroxylation products (ethanol and ethyl trifluoroacetate) and the products of deeper oxidation (acetic acid) dominate in the reaction solutions. The concentration of methyl trifluoroacetate is substantially lower than the concentration of the above oxygenates. The major propane oxidation products (Table 3) are oxygen-containing compounds with three carbon atoms in a chain, propanol, isopropanol, their esters, acetone, and propionic acid. The amounts of products of oxidative destruction



(mainlib) Acetic acid



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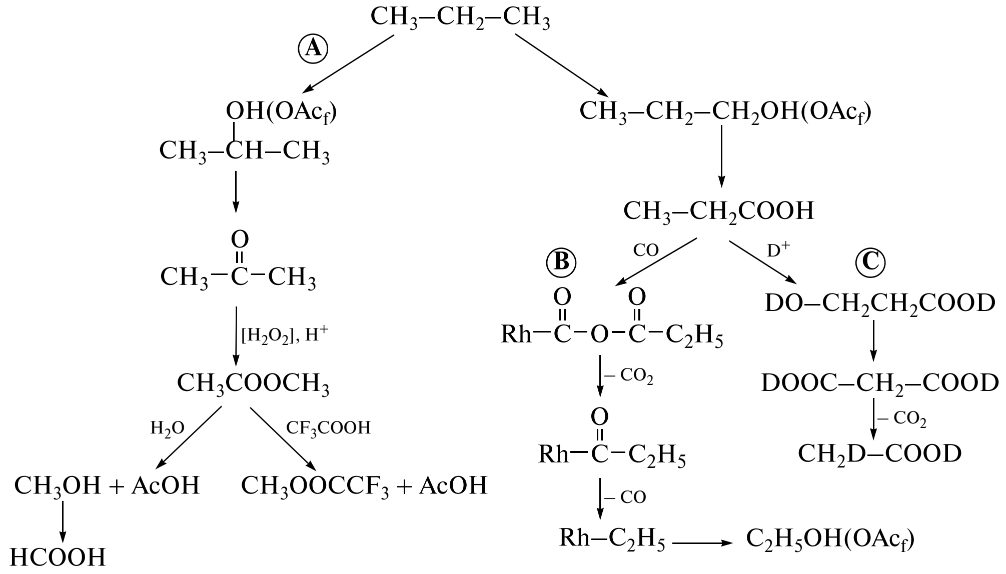
(a) The mass spectrum of acetic acid and (b) the mass spectrum averaged over the chromatographic peak for acetic acid from the reaction solutions of *n*-propane oxidation in the medium of Ac_fOD/D_2O.

(methyl trifluoroacetate, ethyl trifluoroacetate, and acetic acid) are much lower. In the oxidation of *n*-butane, the yield of ethyl trifluoroacetate, methyl trifluoroacetate, and other products of oxidative destruction is substantially higher than the amount of oxygenates without C–C bond cleavage: butyl trifluoroacetates and methyl ethyl ketone (Table 4). The products of isobutane oxidation contain small amounts of isobutyl trifluoroacetate and the others are the products of oxidative destruction, mostly methyl trifluoroacetate and isopropyl trifluoroacetate. In the oxidation of all alkanes, formic acid is also formed in substantial amounts.

One cannot exclude that alkane oxidation with C–C bond cleavage occurs via the mechanism of radical cation $O^{+\cdot}$ transfer from the active oxidant to the substrate [7, 9]. The participation of radical species in alkane oxidation in the Rh–Cu–chloride system is evident from the approximately equal yields of CF_3COOCH_3 and $CF_3COOC_2H_5$ in propane oxidation and CF_3COOCH_3 and $CF_3COO\text{-}i\text{-}C_3H_7$ in isobutane oxidation.

The oxidative destruction of alkanes may also begin with alkane hydroxylation with the formation of primary and secondary alcohols (*n*-propanol and isopropanol in the case of propane oxidation), which are then converted into acids and ketones, as has been found. These compounds can be oxidized with the cleavage of C–C bonds under the same conditions and form the same products as alkanes do (Table 5).

Acetic acid and methanol may be formed in *n*-propane oxidation via the product of isopropanol oxidation (acetone) by the Baeyer–Villiger reaction (Scheme 2, pathway **A**) with the participation of hydrogen peroxide formed by reaction 4 in CO oxidation.



Scheme 2. Pathways of the coupled oxidation of propane and CO by molecular oxygen in the $RhCl_3/Cu(II)/Cl$ catalytic system.

Under reaction conditions, *n*-propanol is oxidized to propionic acid, which then is converted via two pathways: into ethanol and acetic acid. According to [18], the conversion of propionic acid into ethanol (ethyl trifluoroacetate) involves CO insertion into a rhodium–propionate bond and further decarboxylation (Scheme 2, pathway **B**). After the decarboxylation of the propyl complex to form the ethyl complex, its hydrolysis (acidolysis) leads to ethanol (ethyl trifluoroacetate). In the oxidation of propionic acid in $Ac_fOD–D_2O$, deuterated ethanol was not formed, which does not contradict the proposed mechanism. Methanol (methyl trifluoroacetate) is formed analogously in acetic acid oxidation.

The oxidation of propionic acid in $Ac_fOD–D_2O$ solutions leads to acetic acid with a deuterium-substituted methyl group (see figure). Because in the oxidation systems studied alkyl groups do not exchange

Table 1. Oxidative functionalization of methane in the presence of Rh, Pd, and Pt-containing catalytic systems (P_{CH_4} = 6.0 MPa, P_{O_2} = 0.56 MPa, P_{CO} = 1.6 MPa, 80°C, m_{H_2O} = 0.6, $Cu(OAc_f)_2 = 5 \times 10^{-2}$ M, 2 h)

No.	Catalytic system			Products, M × 10^3		
	platinum metal compound, M × 10^3	ligand, M × 10^3	NaCl, M × 10^3	CH_3OAc_f	HCOOH	CH_3COOH
1	$RhCl_3$ (2.5)	–	7.5	102	40	30
2	Na_2PdCl_4 (5.0)	bipy (5.0)	–	71	20	traces
3	Na_2PdCl_4 (5.0)	phen (5.0)	–	66	20	traces
4	Na_2PtCl_4 (5.0)[a]	bipy (5.0)	–	23	10	traces
5	Na_2PtCl_4 (5.0)[a]	phen (5.0)	–	21	10	traces

Note: [a] Pt black precipitation was observed.

Table 2. Oxidation of ethane in the presence of Rh- and Pd-containing systems (12 mmol of ethane was condensed; P_{He} = 3.6 MPa, P_{O_2} = 0.8 MPa, P_{CO} =1.6 MPa, 80°C, m_{H_2O} = 0.5, $Cu(OAc_f)_2 = 5 \times 10^{-2}$ M, 2 h)

No.	Platinum metal c ompound, M × 10^3	Ligand, M × 10	NaCl, M × 10^3	Products, M × 10^3		
				$MeOAc_f$	$EtOAc_f$	AcOH
1	$RhCl_3$ (2.5)	–	7.5	120	53	10
2	Na_2PdCl_4 (5.0)	bipy (5.0)	–	35	11	2

Table 3. Oxidation of propane in the presence of Rh- and Pd-containing catalytic systems (12 mmol of propane was condensed; $P_{He} = 3.6$ MPa, $P_{O_2} = 0.8$ MPa, $P_{CO} = 1.6$ MPa, 80°C, $m_{H_2O} = 0.5$, 2 h; Cu(OAcf)$_2 = 5 \times 10^{-2}$ M)

No.	Platinum metal compound, M × 10^3	Ligand, M × 10^3	NaCl, M × 10^3	Products, M × 10^3					
				$MeOAc_f$	$EtOAc_f$	AcOH	Pr-*i*-OAc_f	$PrOAc_f$	$CH_3C(O)CH_3$
1	$RhCl_3$ (2.5)	–	7.5	65	130	20	560	310	200
2	Na_2PdCl_4 (5.0)	bipy (5.0)	–	35	27		70	35	73
3	K_2PdBr_4 (5.0)	bipy (5.0)	–	traces	traces	traces	10	traces	30
4	$PdBr_4$ (5.0)	bipy (5.0)	–	traces	traces	traces	10	<10	40

Table 4. Oxidation of *n*-butane (12 mmol of *n*-butane was condensed; $P_{He} = 3.6$ MPa, $P_{O_2} = 0.8$ MPa, $P_{CO} = 1.6$ MPa, 80°C, $m_{H_2O} = 0.5$, 2 h, 80°C, $Cu(OAc_f)_2 = 5 \times 10^{-2}$ M)

No.	Catalytic system			Products, M × 10^3						
	platinum metal compound, M × 10^3	ligand, M × 10^3	NaCl, M × 10^3	$MeOAc_f$	$EtOAc_f$	*n*-$PrOAc_f$	sec-$BuOAc_f$	$CH_3C(O)C_2H_5$	*n*-$BuOAc_f$	CH_3COOH
1	$RhCl_3$ (2.5)	–	7.5	150	90	10	15	10	15	90
2	Na_2PdCl_4 (5.0)	bipy (5.0)	–	15	11	8	5	7	4	19
3	$PdBr_2$ (5.0)	bipy (5.0)	–	12	7	3	1	9	2	20

Table 5. Oxidation of compounds that are intermediate products in propane oxidation (conditions are as in Table 3, no. 1; $RhCl_3 = 2.5 \times 10^{-3}$ M; $Cu(OAc_f)_2 = 5 \times 10^{-2}$ M)

No.	Substrate, M	Products, M × 10^3				
		Ac_fOCH_3	$Ac_fOC_2H_5$	AcOH	acetone	C_2H_5COOH
1	*n*-C_3H_7OH[a] (1.06)	40	30	80	–	10
2	C_2H_5COOH (1.04)	30	10	40	–	
3	*iso*-C_3H_7OH[b] (0.99)	50	–	–	230	–
4	Acetone (0.98)	30	–	250		–
5	CH_3COOH (0.98)	20	–		–	–

deuterium with the medium, a possible mechanism of deuterium inclusion in the methyl group of acetic acid is the oxidation of propionic acid to 3-oxyacetic acid and then to malonic acid. The decarboxylation of deuterated malonic acid $DOOCH_2COOD$ leads to the formation of CH_2DCOOD (Scheme 2, pathway **C**)[1].

Thus, at least two mechanisms of alkane conversion with C–C bonds involved are possible: the mechanism with the intermediate formation of radical cations based on alkanes and the mechanism of consecutive oxidation via alcohols, ketones, and acids.

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[1] CHD_2COOD formation can be explained by deuterium exchange between the methylene group of malonic acid and the medium.

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