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Homogeneous Catalytic Oxidation of Light Alkanes: C–C Bond Cleavage under Mild Conditions

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Abstract—The combined oxidation of CO and C_2–C_4 alkanes (associated petroleum gas and natural gas components) under the action of oxygen in trifluoroacetic acid solutions in the presence of rhodium and copper chlorides was accompanied by the oxidative degradation of C–C bonds in a hydrocarbon chain with the formation of carbonyl compounds, alcohols, and esters. For butane and isobutane, the reaction path with C–C bond cleavage was predominant. The buildup curves of isobutane oxidation products (both with the retention and with the degradation of the chain) were S-shaped and characterized by the same induction period; they did not pass through a maximum. A reaction scheme was proposed to reflect the main special features of the mechanism of transformations occurring in the O_2/Rh/Cu/Cl^- oxidation system.

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INTRODUCTION

The literature on the activation and functionalization of C–H bonds in saturated hydrocarbons under mild conditions with the participation of metal complexes is extensive [1–5]. At the same time, there are only a few publications concerning the participation of metal complexes in C–C bond cleavage [6–8]. A promising approach to the activation and oxidation of saturated hydrocarbons consists in a search for catalytic systems analogous to biocatalysts [9], in which a reducing agent is present along with oxygen. Homogeneous catalytic systems consisting of rhodium chloride and cocatalysts (iodine, copper, or iron compounds and alkali metal chlorides) exhibited high activity and stability in the course of the oxidative functionalization of methane under the action of molecular oxygen and carbon monoxide, which served as a reducing agent [10–15]. The oxidation of CO under the action of Rh(III)

$$\mathrm{Rh(III)} + \mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{Rh(I)} + \mathrm{CO_2} + 2\mathrm{H^+},$$

resulted in the formation of Rh(I), which, in turn, can reduce Cu(II) to Cu(I):

$$\mathrm{Rh(I)} + 2\mathrm{Cu(II)} + 2\mathrm{H^+} \longrightarrow \mathrm{Rh(III)} + 2\mathrm{Cu(I)}.$$

Thus, copper in the test system can serve as a reoxidant for catalyst metal. Moreover, the intermediate formation of hydrogen peroxide or other peroxo derivatives on the oxidation of Cu(I) in these systems is hypothesized:

$$2\mathrm{Cu(I)} + 2\mathrm{H^+} + 1/2\mathrm{O_2} \longrightarrow 2\mathrm{Cu(II)} + \mathrm{H_2O};$$
$$2\mathrm{Cu(I)} + 2\mathrm{H^+} + \mathrm{O_2} \longrightarrow 2\mathrm{Cu(II)} + \mathrm{H_2O_2}.$$

The interaction of hydrogen peroxide with Rh(III) results in the formation of a corresponding peroxo complex, and it is believed that the peroxo complexes of rhodium in the highest oxidation states can oxidize methane [15].

It is likely that the role of copper consists in not only the generation of hydrogen peroxide but also the stabilization of an active intermediate [13].

In this study, we found that, in the course of the oxidative conversions of C_2–C_4 alkanes (associated petroleum gas and natural gas components) under conditions of their combined oxidation with CO in the presence of metal complex catalytic systems, the substrates can enter into reactions that lead to C–C bond cleavage.

EXPERIMENTAL

The following chemicals were used: $RhCl_3 \cdot n(H_2O)$ (34.5 wt % Rh), NaCl, CuO (chemically pure), CF_3COOH (chemically pure), D_2O (99.9%), CF_3COOD (99.9%), CO (99.9%), O_2 (99.5%), ethane (99.5%), propane (99.2%), butane (99.9%), isobutane (99.5%), and twice-distilled water. The catalytic experiments were performed in a fluoroplastic-lined autoclave in accordance with a published procedure [10–12].

The qualitative and quantitative analysis of oxidation products was performed by ^1H NMR spectroscopy with the use of an external standard (DMSO in D_2O, capillary) on Bruker A-C200 P (200 MHz) and Tesla BS 587 A (80 MHz) instruments, by gas chroma-

Transformations of C_1–C_4 alkanes in the presence of the $RhCl_3$ (2.5×10^{-3} mol/l) + $Cu(OAc_f)_2$ (5×10^{-2} mol/l) + NaCl (7.5×10^{-3} mol/l) catalytic system in a solution of CF_3COOH–H_2O (2.5 ml) with $m_{H_2O} = 0.6$

Parent alkane	Reaction products, mol/l											
	$HCOOH^c$	Ac_fOMe	AcOH	Ac_fOEt	Ac_fO-*iso*-Pr	Ac_f-*n*-Pr	EtCOOH	$(CH_3)_2CO$	Ac_fO-*iso*-Bu	Ac_fO-*sec*-Bu	Ac_fO-*n*-Bu	$CH_3C(O)C_2H_5$
CH_4^a	0.10	0.15	0.05^d									
$C_2H_6^b$	0.20	0.23	0.02	0.84								
$C_3H_8^b$	0.30	0.07	0.03	0.09	0.24	0.16	0.01	0.15				
n-$C_4H_{10}^b$	0.16	0.32	0.19	0.18		0.01	tr			0.03	0.04	0.02
iso-$C_4H_{10}^b$	0.21	0.24			0.27			0.39	0.02			

[a] Pressure, MPa: CH_4, 6.0; He, 3.6; O_2, 0.56; and CO, 1.84. Temperature: 95°C. Reaction time: 2 h.
[b] Pressure, MPa: He, 3.6; O_2, 0.8; and CO, 1.6. Alkane condensed: ~12 mmol. Temperature: 80°C.
[c] Reaction paths of formic acid formation will be discussed elsewhere.
[d] Acetic acid results from the oxidative carbonylation of methane.

tography (Kristallolyuks 4000M chromatograph equipped with Separon CHN and Separon SDA columns of size 2 m × 3 mm × 0.125–0.200 mm) and gas chromatography–mass spectrometry (GC–MS) (Automass 150 instrument with a CP-Sil column of size 25 m × 0.15 mm × 1.2 μm).

The experiments were performed at the concentrations $[RhCl_3] = 2.5 \times 10^{-3}$ mol/l, $[Cu(II)] = 5 \times 10^{-2}$ mol/l, and $[NaCl] = 7.5 \times 10^{-3}$ mol/l in the $CF_3COOD(CF_3COOH)$–$D_2O(H_2O)$ reaction medium, where the mole fraction of water was m_{H_2O} (or m_{D_2O}) = 0.6, the liquid phase volume was 2.5 cm^3, and the gas phase volume was 31 cm^3. Alkanes were introduced into a cooled reactor by recondensation. The component pressures were the following, MPa: He, 3.6; O_2, 0.56; and CO, 1.84. The table specifies the experimental conditions.

RESULTS AND DISCUSSION

In an aqueous solution of trifluoroacetic acid (Ac_fOH) in the presence of rhodium chloride, potassium iodide or copper (iron) chloride, and sodium chloride, methane under the action of oxygen and carbon monoxide was converted into methanol, methyl trifluoroacetate, formic acid, and acetic acid [10–14]. Both expected oxidation products, in which the carbon skeleton was retained (alcohols or their esters, ketones,[1] and carboxylic acids), and the oxidative degradation products of saturated hydrocarbons were detected upon the oxidation of C_2–C_4 alkanes in the $O_2/Rh/Cu/Cl^-$ system. This was evidenced by the presence of methyl trifluoroacetate (Ac_fOMe), as well as alcohols, ketones, and carboxylic acids whose hydrocarbon chains were shorter than that in the parent alkane, in the reaction mixture.

The ratio between alkane oxidation products with the retention of the carbon skeleton and oxidative degradation products depends on the length and branching of the carbon chain of the hydrocarbon. Thus, upon the oxidation of ethane, hydroxylation products—ethanol and ethyl trifluoroacetate (Ac_fOEt)—and a product of the deep oxidation of ethane (acetic acid) were predominant in reaction solutions (Scheme 1, the table). The concentration of methyl trifluoroacetate was much lower than those of the above oxygenates. In propane oxidation products (Scheme 2, the table), the following oxygen-containing compounds with three carbon atoms in the chains were predominant: propanol and isopropanol, their esters, acetone, and propionic acid. Oxidative degradation products (methyl trifluoroacetate, ethyl trifluoroacetate, and acetic acid) were present in much smaller amounts.

Upon the oxidation of *n*-butane, the yield of ethyl trifluoroacetate, methyl trifluoroacetate, and other oxidative degradation products was much higher than the yield of expected oxygenates—the butyl esters of trifluoroacetic acid and methyl ethyl ketone (Scheme 3, the table). Upon the oxidation of isobutane, only small amounts of isobutyl trifluoroacetate[2]

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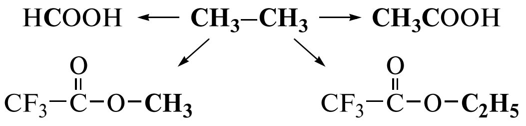
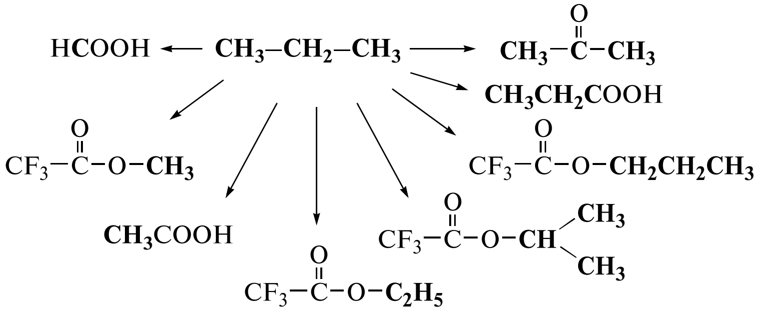
[1] Aldehydes were present in only trace amounts, probably, because of rapid oxidation.

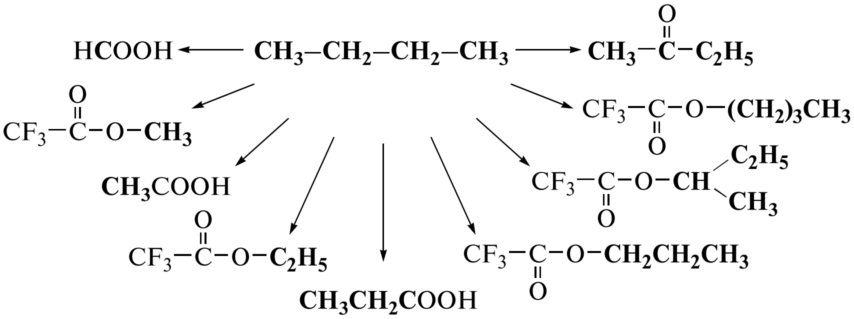
[2] The amount of *tert*-butyl trifluoroacetate was even smaller; however, it was reliably identified by GC–MS analysis.



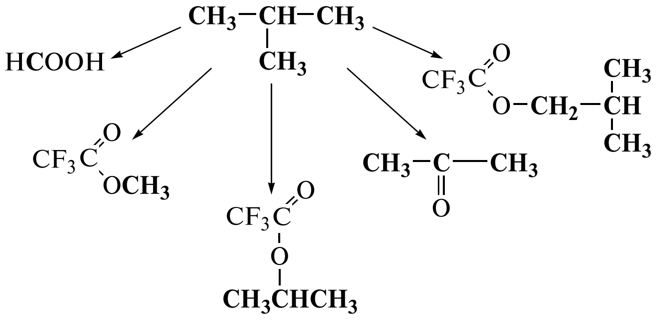
Scheme 1. Ethane oxidation products.



Scheme 2. Propane oxidation products.



Scheme 3. *n*-Butane oxidation products.

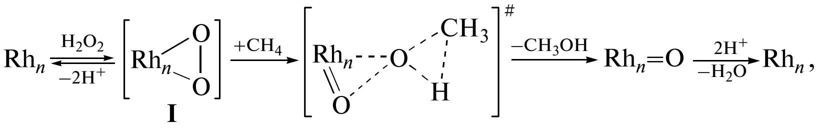


Scheme 4. Isobutane oxidation products.

were detected in reaction solutions; the other components were oxidative degradation products (Scheme 4, the table).

The kinetic curves of the buildup of all the isobutane oxidation products (with both retained and degraded chains) were S-shaped; they exhibited the same induction period (see the figure) and did not pass through a maximum. This suggests that the substrate hydroxylation product and oxidative degradation products (methyl trifluoroacetate and isopropyl trifluoroacetate) were simultaneously formed in substrate reactions with an active oxidizing agent through a common intermediate because the formation of at least two different active oxidizing agents at the same rate would otherwise be hypothesized. In terms of the proposed model, the occurrence of an induction period was due to the formation of an active intermediate responsible for the oxidation of hydrocarbons.

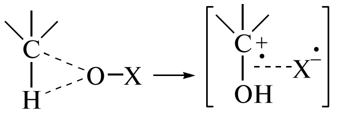
Previously, it was found that rhodium peroxo complex (**I**) participates in the hydroxylation of methane in the test system [15]:



where $2 < n < 4$.

The key step of this reaction is the insertion of an oxygen atom into a C–H bond of the alkane. It is believed that this complex is also responsible for the hydroxylation of C_2–C_4 alkanes. However, the formation of carbonyl compounds or compounds with a shortened hydrocarbon chain cannot be explained in terms of this mechanism.

The high electronegativity of the Rh_n=O leaving group of the complex allows us to hypothesize that complex (**I**), which is shown in Eq. (I) as X–O, can transfer not only an oxygen atom but also an oxygen radical cation (in this case, the oxidation number of rhodium decreases by unity) to the substrate with the formation of a tight ion pair without the escape of the free radical cation into the bulk:



I **II**

(I)

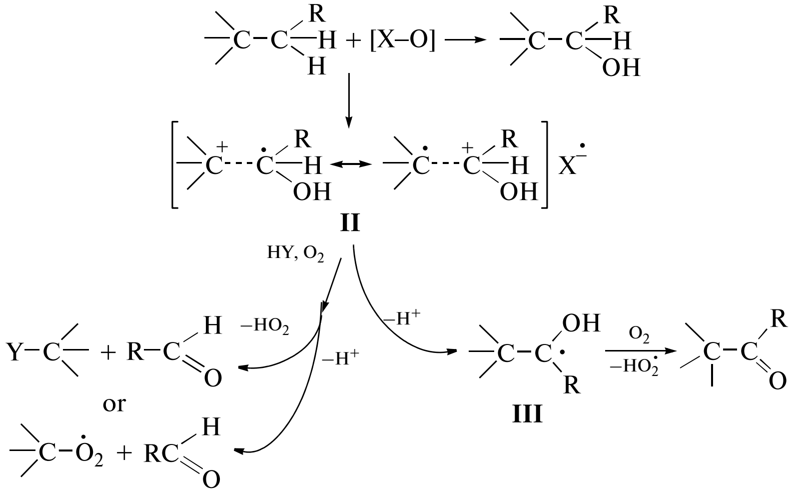
where X = Rh_n=O.

Upon the formation of a radical cation, an electron is removed from the highest occupied molecular orbital (from a σ-bonding orbital in the case of an alkane) to weaken the C–C bond. Thus, the radical cation can react both with C–C bond cleavage and with the retention of the molecular hydrocarbon skeleton. In resulting ion–radical pair **II**, a positive charge and an unpaired electron are localized at different carbon atoms. Thus, it is likely that, after proton elimination, complex **II** undergoes oxidation through the intermediate formation of radical **III** to form a carbonyl compound (Scheme 5).

At the same time, **II** can react with a nucleophilic particle and molecular oxygen; in this case, the direction of a nucleophilic attack of water or carboxylic acid depends on the predominant localization of a positive charge, whereas the function of molecular oxygen is hydrogen atom abstraction from a carbon atom at which an unpaired electron is mainly localized. In this case, a C–C bond is cleaved (Scheme 5).

It is likely that the oxidation of alkanes in the $O_2/Rh/Cu/Cl^-$ catalytic system occurs via several reaction paths; this fact can explain the variety of products.

It is reasonable to hypothesize the mechanism of C–C bond cleavage in alkanes. Thus, for example, ethane and propane conversions were observed at 180°C in the course of a stoichiometric reaction of



X–O is an oxidant, Y = OH or AcO

Scheme 5. Hypothetical mechanism of oxidative C–C bond degradation.

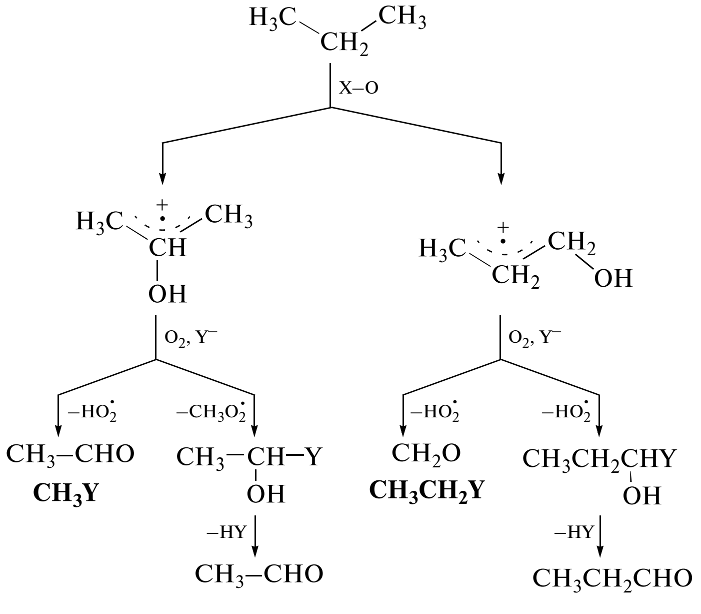
cobalt(III) trifluoroacetate or a catalytic reaction of cobalt(II) trifluoroacetate in the presence of oxygen (4 MPa) [6]. It is believed that the process begins with electron abstraction from a hydrocarbon. The resulting radical cation decomposes with C–C bond cleavage to form organic cations and radicals. A carbon-centered radical is converted into a cation under the action of cobalt(III). The cations react with trifluoroacetic acid to form esters, which were detected as product constituents. The initial formation of radical cations was also hypothesized in a discussion of the results of experiments in which hydrocarbons were oxidized at C–C bonds in a rhodium–iodide–chloride system [7]. However, Lin et al. [7] gave preference to a molecular mechanism with the participation of the inner coordination sphere of rhodium. Interesting hydrocarbon transformations were observed on peroxide oxidation in the presence of vanadium complexes [8]. Only branched alkanes underwent oxidation at the R–CH_3 bond. Stolyarov with coauthors [6, 8] explained the oxidative cleavage of C–C bonds by the considerable weakening of these bonds in radical cations. A molecular mechanism of C–C bond cleavage was established in the stoichiometric oxidation of cyclohexane on an OsO_4 catalyst in water. It is likely that, at pH 12, the C–C bond was cleaved at *cis*-oxo groups of osmium tetraoxide according to a [3+2] mechanism [16].

Thus, we can hypothesize that, in the presence of the rhodium–copper–chloride catalytic system, C–C bonds are activated as a result of electron trapping at the electrophilic fragment of a catalytically active intermediate (rhodium peroxo complex) [15]. Approximately the same yields of CF_3COOCH_3 and $CF_3COOC_2H_5$ from propane and CF_3COOCH_3 and CF_3COO-*iso*-C_3H_7 from isobutane evidence of the participation of reactive radical cations in the reaction because, in terms of the reaction scheme under consideration, the resulting radical cation in the presence of oxygen reacts in accordance with Scheme 6.

A tight cation–radical pair results from interaction with an active intermediate that is responsible for the insertion of O^+ into an alkane C–H bond (reaction (I)). Undoubtedly, the methylene group is more reactive than the methyl group; however, the number of hydrogen atoms in the methylene group of a propane molecule is smaller than that in methyl groups by a factor of 3. Thus, we can hypothesize that intermediate cation–radical pairs with the participation of CH_2 and CH_3 groups are formed in commensurable amounts to provide the commensurable yields of methanol and ethanol and/or their esters.

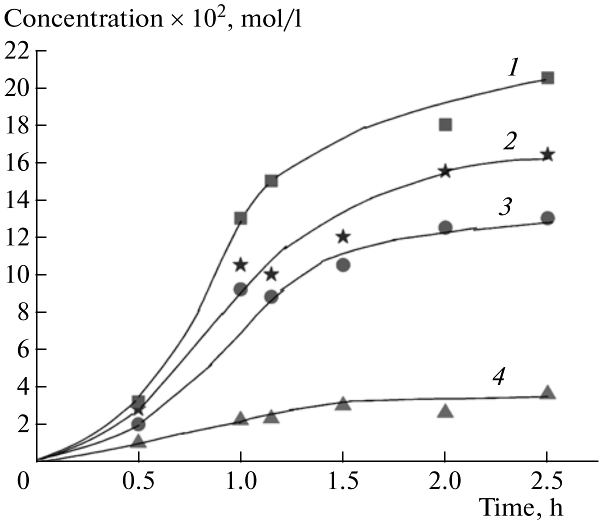
The resulting peroxide radicals $HO_2^{\bullet}$ and $CH_3O_2^{\bullet}$ cannot initiate and run a chain process because of rapid disproportionation and reduction to a hydroperoxide in the presence of copper(I) ions in the former and latter cases, respectively.

The C_4 hydrocarbons are more prone to oxidative degradation at C–C bonds than ethane and propane; this is likely due to the better stabilization of intermediate radical cation species. On the other hand, the process can begin with the activation of a C–H bond and the formation of primary and secondary alcohols, which are subsequently oxidized to acids and ketones, as found previously. We found that acids and ketones are oxidized at C–C bonds under the same conditions and with the formation of the same products as those



X–O is an oxidant, Y = OH or AcO

Scheme 6. Hypothetical mechanism of propane oxidation with C–C bond degradation.



Isobutane oxidation (according to ^{1}H NMR-spectroscopic data) with the formation of (*1*) HCOOD, (*2*) Ac$_f$O-*iso*-Pr + *iso*-PrOD, (*3*) Ac$_f$OCH$_3$, and (*4*) Ac$_f$O-*iso*-Bu + *iso*-BuOD. Reaction conditions: [RhCl$_3$] = 2.5×10^{-3} mol/l; reaction medium, CF$_3$COOD–D$_2$O, $m_{D_2O} = 0.6$; temperature, 95°C; [NaCl] = 7.5×10^{-3} mol/l; [Cu(II)] = 5×10^{-2} mol/l; iso-BuH volume, 285 cm^3; O$_2$, CO, and He pressures, 0.56, 1.84, and 4.0 MPa, respectively. The buildup curve of acetone is not shown because a broadened ^{1}H NMR signal is difficult to integrate.

in the case of alkanes. For example, acetone is oxidized to HCOOH, CF_3COOCH_3, and CH_3COOH, and propionic acid is oxidized to HCOOH, CF_3COOCH_3, $CF_3COOC_2H_5$, and CH_3COOH. Therefore, it is likely that reaction paths with the consecutive oxidation of alkanes into products with shortened chains through alcohols, ketones, and acids can occur.

Thus, in this work, we found that oxygenates with a shortened hydrocarbon chain are formed under mild conditions upon the oxidation of C_2–C_4 alkanes in the presence of the Rh/Cu/Cl$^-$ catalytic system under the action of molecular oxygen and carbon monoxide along with the expected products of substitution for hydrogen atom (alcohols, ketones, and acids).

The results of a systematic study of the reactivity of C–C bonds in structurally different saturated hydrocarbons in the presence of the developed catalytic systems will be published elsewhere.

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