Kinetics and Catalysis, Vol. 45, No. 1, 2004, pp. 40–60. Translated from Kinetika i Kataliz, Vol. 45, No. 1, 2004, pp. 45–66.
Original Russian Text Copyright © 2004 by Gekhman, Stolyarov, Ershova, Moiseeva, Moiseev.

Hydroperoxide Oxidation of Difficult-to-Oxidize Substrates: An Unprecedented C–C Bond Cleavage in Alkanes and the Oxidation of Molecular Nitrogen[1]

A. E. Gekhman*, I. P. Stolyarov*, N. V. Ershova*, N. I. Moiseeva, and I. I. Moiseev***
** Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 117907 Russia*
*** Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia*

Received December 20, 2002

Abstract—In the $V^{(V)}H_2O_2$/AcOH system, C_5–C_{20} *n*-alkanes, isooctane, and neohexane undergo oxidation to ketones and alcohols; the oxidation products of branched alkanes are indicative of a C–C bond cleavage in these substrates. A concept is developed, according to which the peroxo complexes of vanadium(V) are responsible for alkane oxidation. These complexes can transfer the oxygen atom or the $O^{+\bullet}$ radical cation to a substrate. The formation of nitrous oxide was found in the oxidation of molecular nitrogen in the $H_2O_2/V^{(V)}/CF_3COOH$ system.

INTRODUCTION

The oxidation of alkanes by hydroperoxides in the presence of transition metals has been known since the report of Fenton [1]; as a rule, it occurs via a radical chain mechanism. However, the reactivity of hydroperoxides and metal complexes depends on the nature of the solvent, the metal, and the ligand environment [2–4]. Thus, the use of metals with the d^0 nonbonding configuration opens up possibilities for the molecular paths of peroxide activation [2–5].

In carboxylic acid media containing vanadium(V) compounds, the one-electron reduction of the central atom by hydrogen peroxide is not the main reaction path of H_2O_2 decomposition in the absence of ligands that stabilize vanadium(V) [6, 7].

It is well known that vanadium(V) compounds in AcOH catalyze H_2O_2 decomposition with the formation of singlet dioxygen (reaction (I)) and small amounts of ozone (reaction (II)) in addition to $^3O_2$ [8–11]:

$$2H_2O_2 \longrightarrow 2H_2O + {}^1O_2, \qquad \text{(I)}$$

$$3H_2O_2 \longrightarrow 2H_2O + O_3. \qquad \text{(II)}$$

The simultaneous decomposition of AcOOH and H_2O_2 in an AcOH solution in the presence of vanadium(V) complexes is the oxidation of H_2O_2 by AcOOH, which is a stronger oxidizing agent [12],

$$H_2O_2 + AcOOH \longrightarrow O_2 + H_2O + AcOH.$$

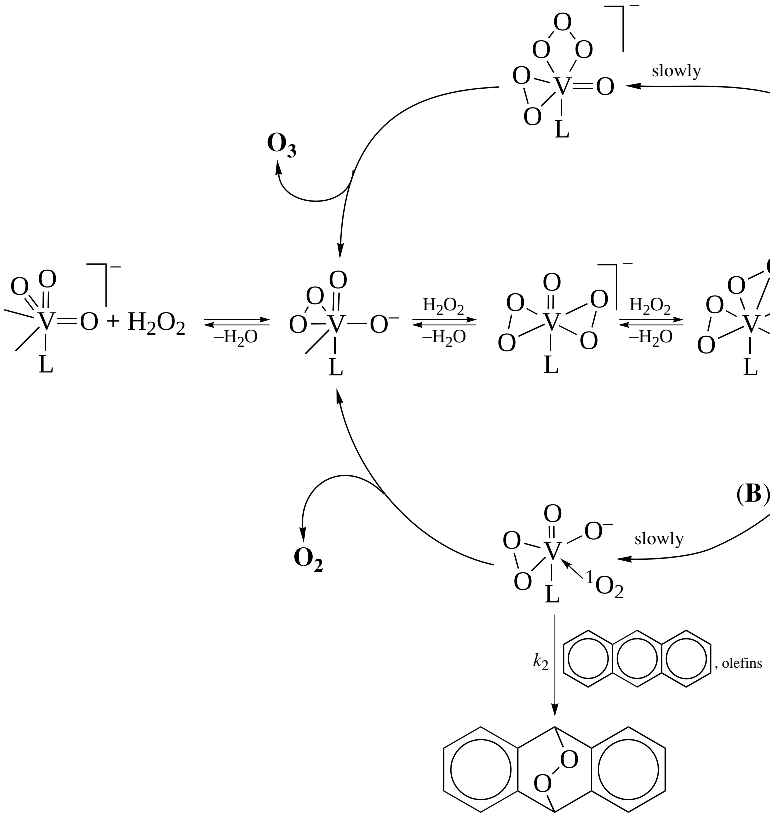
In a discussion of the nature of conceivable oxidizing agents responsible for reactions with organic substrates in the $V^{(V)}/H_2O_2$/AcOH system, a number of vanadium(V) complexes should be considered. These complexes appear in the course of hydrogen peroxide decomposition in this system and include from one to four peroxo groups O_2^{2-} depending on the reaction conditions [13–19]. Some of these complexes, such as monoperoxo ($[(O)_2V^{(V)}(O_2)]^-$) and diperoxo complexes ($[O{=}V^{(V)}(O_2)_2]^-$), were detected on the decomposition of H_2O_2 in AcOH with the use of NMR spectroscopy of vanadium nuclei [6, 7].[2] Moreover, kinetic data are indicative of the intermediate formation of a complex with three peroxo groups, $[V^{(V)}(O_2)_3]^-$, which is converted into a vanadium(V) complex with singlet dioxygen at a rate-limiting step [9–11].[3] Singlet dioxygen is responsible for the oxidation of anthracene and its derivatives to corresponding anthraquinones and for the oxidative degradation of olefins to the corresponding carbonyl compounds [6, 7, 9, 10, 20–23] (Scheme 1). Within the framework of this scheme, a mechanism was proposed for ozone formation; this mechanism includes the intermediate for-

---

[1] Based on the plenary lecture delivered by A.E. Gekhman, corresponding member of the Russian Academy of Sciences, at the VI Russian Conference “Catalytic Reaction Mechanisms” (October 1–5, 2002, Moscow).

[2] There is no data on the composition of the coordination sphere, except for kinetic or spectroscopic evidence of O^{2-} and O_2^{2-} ligands. Therefore, the other ligands are omitted from the formulas of the complexes. It is likely that H_2O or AcOH molecules occupy vacant sites in the coordination sphere of vanadium(V).

[3] Henceforth, the term vanadium(V) complex with singlet dioxygen refers to an intermediate responsible for the transfer of the $^1O_2$ species to a substrate.



Scheme 1. Mechanism of H_2O_2 decomposition with the formation of ozone.

mation of a vanadium(V) complex with the trioxo ligand O_3^{2-} before a rate-limiting step [9, 10].

The oxidation of saturated substrates such as cyclohexane and cyclopentane, which are not prone to reactions with ozone and singlet dioxygen, results in corresponding cycloalkanols and cycloalkanones [24].

A wide variety of active oxidizing agents in the $V^{(V)}/H_2O_2/AcOH$ system complicates the mechanistic studies of reactions that occur in this system. In this work, in order to reveal the nature of processes that form the basis of alkane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system, we studied the reactions of normal alkanes (C_5–C_{20}), isoalkanes (2,2,4-trimethylpentane (isooctane), 2-methylbutane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane (neohexane)), fatty acid methyl esters, and molecular nitrogen. The results of this study are compared to previous data on cyclohexane oxidation.

EXPERIMENTAL

Materials

The following chemicals were used without preliminary purification: glacial acetic acid (chemically pure), hydrogen peroxide (analytical grade, a 16.2 mol/l aqueous solution), commercial trifluoroacetic acid, linear alkanes (pentane, hexane, heptane, octane, nonane, dodecane, hexadecane, and eicosane, all of 98% or better purity according to GLC analysis), isooctane (reference, GOST 4374-48), 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane (98–99%, Aldrich), NH_4VO_3 (chemically pure), bis(trimethylsilyl)trifluoroacetamide (BSTFA, Merck), methanol (chemically pure), $LiAlH_4$ (pure), ionol (2,6-di-*tert*-butyl-4-methylphenol, chemically pure), and molecular nitrogen (high-purity grade). Commercial $VO(acac)_2$ was purified by recrystallization from $CHCl_3$. Fatty acid methyl esters (FAMEs) were synthesized from the corresponding carboxylic acids (all of 98% or better purity according to GLC analysis) according to a published procedure [25].

Preparation of a Catalyst Solution

To prepare an AcOH solution containing vanadium(V) compounds, 100 mg of finely ground NH_4VO_3 was refluxed in 100 ml of AcOH for 4–5 h. Undissolved NH_4VO_3 was filtered off. According to ICP MS data, the concentration of vanadium(V) in solution was 3.7×10^{-3} mol/l. The ICP MS spectra were measured on an HP 4500 ICP MS instrument (an aqueous solution of NH_4VO_3 was used as an external standard). In some kinetic experiments, $VO(acac)_2$, which is more soluble in AcOH, was used as the starting compound for a catalyst. According to EPR data, the signal of $V^{(IV)}$ from $VO(acac)_2$ disappeared immediately after the addition of the first portion of H_2O_2. The replacement of $VO(acac)_2$ by NH_4VO_3 had no effect on the composition and distribution of reaction products and on the rate of the reaction.

Experimental Procedure for Oxidation and Analysis of Products

The oxidation of linear and branched alkanes and FAMEs was performed in a thermostatted jacketed glass reactor with a magnetic stirrer at 30°C. In a typical experiment, 0.3 ml (4.86 mmol) of aqueous H_2O_2 (16.2 mol/l) was added to a solution of $VO(acac)_2$ (5 mg, 0.019 mmol) and *n*-hexane (43 mg, 0.5 mmol) in 5 ml of glacial acetic acid. The decomposition of H_2O_2 was monitored by iodometry. The conversion of substrates and the yields and compositions of reaction products were determined by GLC and gas chromatography–mass spectrometry (GC–MS).

To determine the substrate conversion, 0.1 ml of an internal standard solution (0.1 mol/l acetonitrile in acetic acid) was added to 0.1 ml of the reaction mixture. The resulting mixture (0.5 μl) was analyzed by chromatography.

Sample preparation for the identification of alkane oxidation products was performed as follows: After the complete consumption of H_2O_2, 1 ml of $CHCl_3$ (or diethyl ether) and 5 ml of water were added to 1 ml of the reaction mixture. The organic phase was separated, washed with a 5% aqueous Na_2CO_3 solution (1 ml) and water (1 ml), and analyzed by chromatography.

The above procedure for the extraction of reaction products from reaction solutions did not allow us to determine quantitatively the concentrations of all components because it is impossible to extract completely water-soluble components (such as ethanol and 2-propanol) from aqueous solutions into diethyl ether. In experiments with isooctane, the above sample preparation process was changed. After the extraction of oxidation products with diethyl ether, the resulting extract was concentrated by slowly evaporating the ether at ~20°C in a flow of nitrogen; this prevented the evaporation of highly volatile components as far as possible.

For the analysis of FAME oxidation products, a 1-ml sample was diluted with 5 ml of water and extracted with 1 ml of chloroform. The extract was dried with Ca5A molecular sieves, and 0.1 ml of BSTFA was added to the dry solution. The mixture was placed in an airtight microreactor and held at 60°C for 1 h to perform silylation. The resulting solution was examined by GC–MS.

2-Propanol, 2-methyl-2-propanol, 2-butanol, 2-butanone, 2-methyl-1-propanol, and ethyl acetate from a reaction mixture were separated with the use of chromatographic columns of different polarity and identified by coincidence between the chromatographic retention times and mass spectra of sample components and standard substances.

To study complex mixtures (in the case of 3-methylpentane or isooctane oxidation), a solution of oxidation products in diethyl ether was exposed to $LiAlH_4$ for the exhaustive reduction of ketones and esters to the corresponding alcohols. Based on a subsequent comparison of the chromatograms of initial and reduced samples obtained using chromatographic columns of different polarity, as well as the mass spectra, conclusions on the structures of sample components were made. In the cases when the retention times and mass spectra of components were similar (for example, for 2,4,4-trimethyl-1-pentanol and 2,2,4-trimethyl-1-pentanol), an alpha-Dex 120 enantioselective chromatographic column was used. Because oxidation is not enantioselective and, of the above two isomers, only 2,4,4-trimethyl-1-pentanol has an asymmetric center, the chromatogram of this alcohol exhibits two chromatographic peaks with equal intensities, and the mass spectra of these peaks are identical.

An AUTOMASS 150 GC–MS instrument (Delsy Nermag, France) was used for obtaining mass spectra under the following conditions: $EI = 70$ eV; the ion source temperature was 100°C; the mass spectrometer was adjusted using FC43 (reference peaks of m/z 18, 28, 69, 100, 131, 219, 264, 414, and 502); the spectrum range was 30–300 amu; the scan time was 300 ms; a fused-silica capillary column (0.25 mm × 25 m; d_f = 0.3 μm) (Rescom) with OV-1, CPWax-58, or alpha-Dex 120 was used; the split ratio was 1/40; P_{inj} = 0.6 atm (at T_{col} = 50°C); He; T_{inj} = 250°C. The Lucy (ver. 2.10) and AMDIS (ver. 2.1) software and the NIST mass-spectral database (1987, 1995) were used for GC–MS data acquisition and processing.

As an example, Fig. 1 demonstrates a portion of the chromatogram of isooctane oxidation products. Figure 2 illustrates the identification of one of the oxidation products with a retention time of 159 s (4,4-dimethyl-2-pentanol) with the use of a reference spectrum (from the NIST mass-spectral database (1987, 1995)).

The quantitative GLC analysis of the initial substances and oxidation products was performed on a 3700 chromatograph (Russia) equipped with an HP-1 capillary column (0.25 mm × 25 m; d_f = 0.3 μm); the split ratio was 1/40; P = 1 atm (at $T_{initial}$ = 50°C); He; $T_{initial}$ was varied depending on the substrate; the heating rate was 10 K/min; T_{final} = 250°C; FID. An L-241 analog-to-digital converter (20 bit) and the Multichrom 1.39 software (Ampersand Ltd) were used for chromatographic data acquisition and processing.

Table 1 summarizes the internal standards and T_{inj} for the GLC analysis of oxidation products of various substrates.

The GLC analysis of the starting isooctane (analytical grade) was performed on a 3700 chromatograph (Russia) equipped with an SPB-1 capillary column

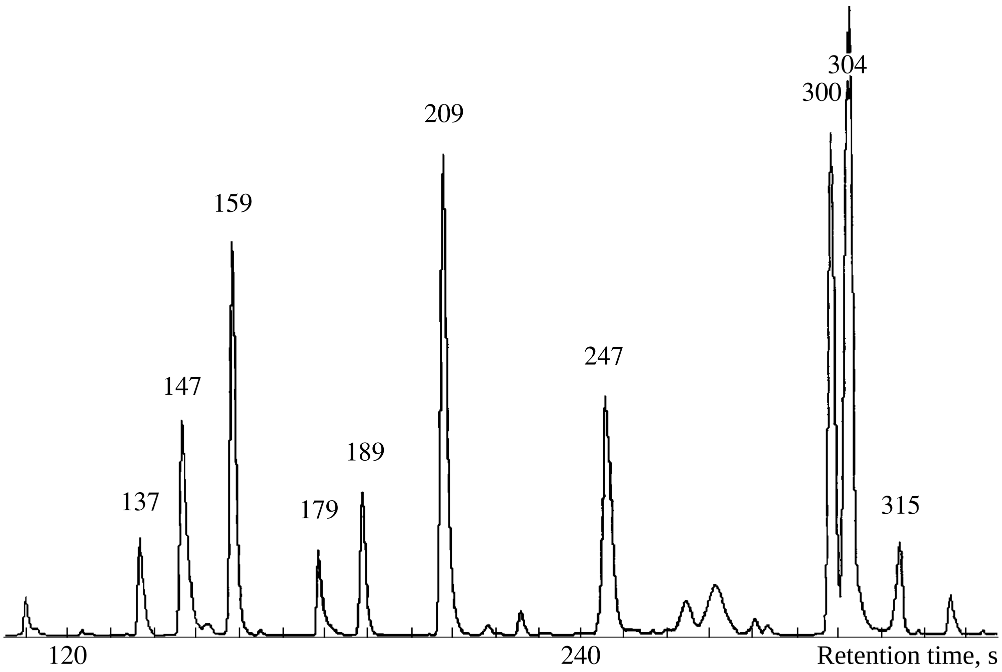


Fig. 1. Chromatogram of a chloroform extract of the reaction mixture of isooctane oxidation in the $V^{(V)}/H_2O_2$/AcOH system, 30°C; $[V^{(V)}] = 4 \times 10^{-3}$ mol/l; $[Sub]_0 = 0.1$ mol/l; $[H_2O_2]_0 = 1$ mol/l.

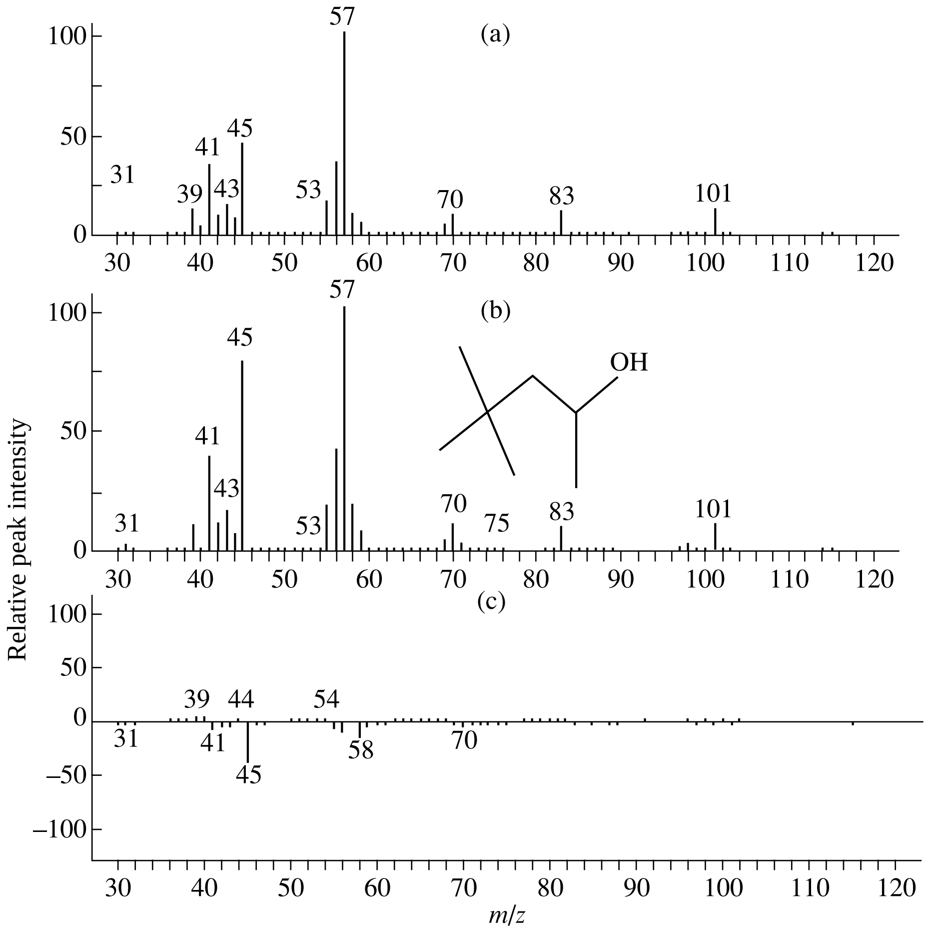
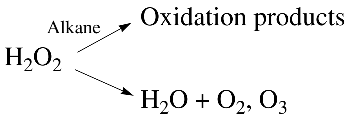


Fig. 2. (a) Mass spectrum corresponding to the chromatographic peak with a retention time 159 s in Fig. 1, (b) the reference mass spectrum of 4,4'-dimethylpentanol, and (c) difference between the spectra.



Scheme 2. Reaction paths of hydrogen peroxide consumption under conditions of *n*-alkane oxidation.

(0.25 mm × 100 m; $d_f = 0.25$ μm) (Supelco); the split ratio was 1/40; $P = 0.32$ atm; $T_{inj} = 250$°C; and $T_{col} = 60$°C. According to GLC data, the isooctane purity was 99.86 ± 0.04%. The following impurities were identified based on the retention times: 2,3-dimethylpentane (0.06%), 3-ethylpentane (0.02%), and 2,2-dimethylhexane (0.05%) [26]. The total concentration of other impurities was no higher than 0.01%.

The oxidation of N_2 was performed by passing a flow of N_2 (30–60 ml/min) through a reactor with a solution of H_2O_2 (1 mol/l) and $VO(acac)_2$ (10^{-2} mol/l) in trifluoroacetic acid at 0–20°C. The gas mixture was collected for 5–20 min over an aqueous NaCl or NaOH solution and analyzed by GC–MS under the following conditions: AUTOMASS 150 GC–MS instrument; Supel-QPlot column (30 m × 0.32 mm) (Supelco); –10°C; $P_{inj} = 0.5$ atm; split ratio of 1/40; sample volume of 100 μl; $EI = 70$ eV; mass range of 25–100 amu; and scan time of 50 ms.

RESULTS AND DISCUSSION

Oxidation of Linear Alkanes

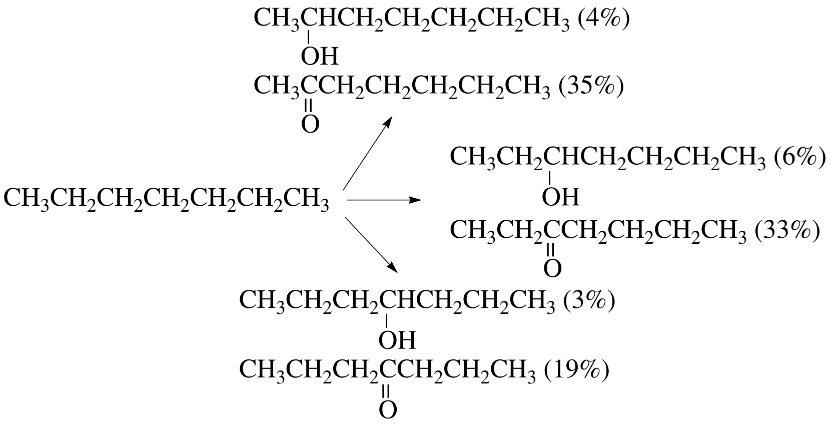
Normal C_5–C_{20} alkanes and branched C_6–C_8 alkanes were chosen as substrates for comparing their reactivity with that of cyclohexane [24]. In the absence of a catalyst from an H_2O_2/AcOH solution, no detectable consumption of the above substrates at room temperature within several hours was found, as well as in the oxidation of cyclohexane. After the addition of a catalyst (~10^{-2} mol/l), the consumption of H_2O_2 began, which was practically complete after ~1 h at 30°C. The amount of oxidized alkane depended on the initial H_2O_2 concentration ($[H_2O_2]_0$) and monotonically increased as this concentration was increased (Fig. 3). More than a tenfold excess of H_2O_2 was required for attaining ~90% conversion of an alkane because hydrogen peroxide was consumed in at least two parallel reaction paths (Scheme 2); in this case, the major portion of H_2O_2 decomposed into H_2O and O_2.

In terms of Scheme 2, the higher the reactivity of an alkane, the higher its conversion, all other factors ($[H_2O_2]_0$ etc.) being the same. It follows from Fig. 3 that the reactivity of *n*-alkanes somewhat decreases with carbon chain length in the order pentane > hexane > decane > dodecane.

Secondary alcohols and ketones with carbon chain lengths equal to the chain length of the starting hydrocarbon were detected in hydrocarbon oxidation products (Table 2). The oxidation of linear alkanes affects only C_{sec}–H bonds, and it is accompanied by neither the oxidative degradation of the substrate nor the oxidation of terminal methyl groups. Thus, 2-heptanol, 3-heptanol, 4-heptanol, 2-heptanone, 3-heptanone, and 4-heptanone were detected in the oxidation of *n*-heptane (Scheme 3). Neither 1-heptanol nor heptanal was detected in the oxidation products of *n*-heptane. The products of skeletal isomerization were also not found.

The total yield of alcohols and ketones was no higher than 60% at a substrate conversion of ~35%. The ketone content of oxidation products was much higher than the alcohol content (Table 2). Keto alcohols were not found among the oxidation products of *n*-heptane and lower alkanes.

The buildup of ketones and alcohols in the oxidation of alkanes (Fig. 4) occurs without an induction period; the kinetic curves exhibit no singular points. Traditional free-radical reaction inhibitors, such as ionol and *para*-benzoquinone, have no effect on the composition of alkane oxidation products (Table 2, nos. 1, 2) or the shape of the kinetic curve. The yield of oxidation products, the ratio [ketone]/[alcohol], and the yield of posi-



Scheme 3. Identified products of *n*-heptane oxidation in the $V^{(V)}/H_2O_2$/AcOH system (relative product yields are given in parentheses).

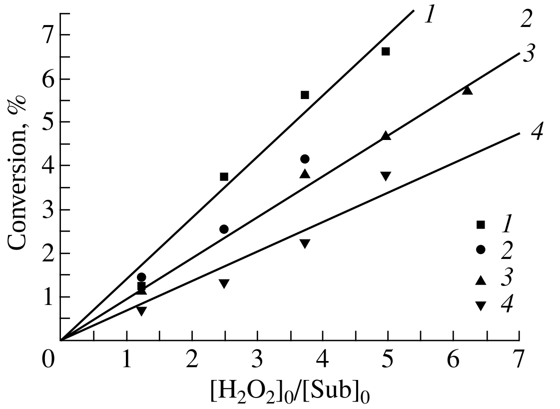


Fig. 3. Limiting *n*-alkane conversion as a function of $[H_2O_2]_0/[Sub]_0$ in the oxidation of (*1*) *n*-pentane, (*2*) *n*-hexane, (*3*) *n*-decane, or (*4*) *n*-dodecane.

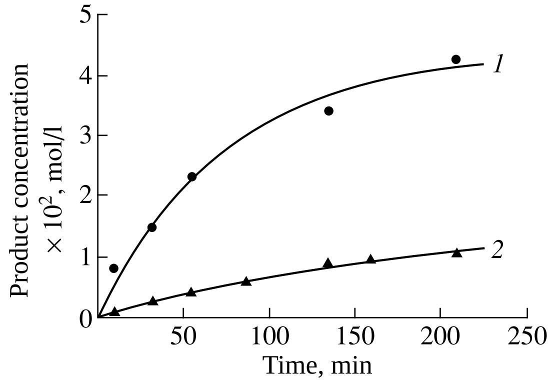


Fig. 4. Accumulation of (*1*) pentanones and (*2*) pentanols in the oxidation of *n*-pentane in the $V^{(V)}/H_2O_2/AcOH$ system; 30°C; $[V^{(V)}] = 4 \times 10^{-3}$ mol/l; $[Sub]_0 = 0.1$ mol/l; $[H_2O_2]_0 = 1$ mol/l.

tional isomers are also independent of the presence or absence of an inhibitor. These data exclude a free-radical chain mechanism of alkane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.

It would be assumed that ketones, the amount of which is greater than the amount of alcohols, are formed in the consecutive oxidation reactions alkane ⟶ alcohol ⟶ ketone. To test this hypothesis, we studied the simultaneous oxidation of *n*-octane and 3-pentanol. In the simultaneous oxidation of 3-pentanol (0.01 mol/l) and *n*-octane (0.1 mol/l) at $[H_2O_2]_0 = 1$ mol/l, the conversion of 3-pentanol was negligibly small. In experiments when 2-butanol (0.01 mol/l) was oxidized simultaneously with *n*-octane (0.1 mol/l), the final concentration of 2-butanone was no higher than 0.001 mol/l even after the complete decomposition of H_2O_2 ($[H_2O_2]_0 =$ 1 mol/l). All these facts suggest that alcohols are not intermediates in the formation of ketones. Alcohols and ketones are formed in parallel reactions, and they are the final products of alkane oxidation.

The following similarities between the oxidation of linear alkanes and cyclohexane are clear:

(1) The hydrocarbon skeleton remains unaffected by oxidation.

(2) All the test substrates are oxidized to the corresponding alcohols and ketones.

Table 1. Conditions of the GLC analysis of oxidized substrates

Substrate	Internal standard	T_{inj}, °C
C_5–C_{10} *n*-alkanes	MeCN	50–70
C_{11}–C_{22} *n*-alkanes	PhCN	100
C_3–C_8 FAMEs	*n*-decane	80
C_9–C_{18} FAMEs	*n*-hexadecane	100

(3) Alcohols and ketones are formed in parallel reactions.

(4) Linear alkanes and cyclohexane are oxidized by a nonchain mechanism.

All these data allow us to consider the oxidation of cyclohexane and acyclic alkanes in terms of a single mechanism with the participation of the same active intermediates. This provides an opportunity to reveal the relative reactivities of lower linear alkanes and cyclohexane by studying their competitive oxidation.

If the same vanadium complex is responsible for the oxidation of both alkanes and cyclohexane, the ratio between the rate constants of substrate reactions with an active intermediate can be calculated from the equation [27]

$$\frac{k_A}{k_{\text{cyclohexane}}} = \frac{\ln(100 - x_A)}{\ln(100 - x_{\text{cyclohexane}})},$$

where x_A and $x_{\text{cyclohexane}}$ are the degrees of conversion of linear alkanes and cyclohexane, respectively.

We found that the relative rate constants of oxidation of linear alkanes and cyclohexane lie in the range 0.6–1.7; that is, the reactivity of *n*-alkanes, except for *n*-pentane, is commensurable with the reactivity of cyclohexane in the test reaction (Table 3).[4] Because there is no experimental or theoretical evidence for the formation of a strong vanadium(V)/hydrocarbon complex [28, 29], all differences in reactivity should be related to the interaction of an active vanadium complex with a substrate.

Similar values of the rates of oxidation of linear alkanes and cyclohexane and the similarity between their transformations in the $V^{(V)}/H_2O_2/AcOH$ system

---

[4] The consumption of low-boiling *n*-pentane can be somewhat overestimated because of its removal from the reactor with a flow of oxygen released on the decomposition of hydrogen peroxide (the reaction temperature is 30°C, and the boiling temperature of *n*-pentane is somewhat higher and equal to 35–36°C).

Table 2. Oxidation of *n*-alkanes in the $V^{(V)}/H_2O_2/AcOH$ system

No.	Substrate (Sub)	$[Sub]_0$, mol/l	Conversion, %	$[Alcohol]_\Sigma \times 10^4$, mol/l	$[Ketone]_\Sigma \times 10^3$, mol/l
1	*n*-pentane	0.10	49	45[a]	40[b]
2	*n*-pentane + ionol	0.10	47	43	38
		0.01	–	–	–
3	*n*-hexane	0.10	32	37[c]	25[d]
4	*n*-heptane	0.10	32	24[e]	18[f]
5	*n*-octane	0.10	30	32[g]	20[h]
6	*n*-nonane	0.05	31	18	9[i]
7	*n*-decane	0.05	29	22	8
8	*n*-tetradecane	0.05	21	33	6
9	*n*-pentadecane	0.05	16	23	5
10	*n*-hexadecane	0.05	15	18	5
11	*n*-nonadecane	0.05	11	21	3

Note: 30°C; $[V^{(V)}] = 4 \times 10^{-3}$ mol/l; $[H_2O_2]_0 = 1$ mol/l.

[a] [2-pentanol]/[3-pentanol] = 1.6/1.

[b] [2-pentanone]/[3-pentanone] = 1.9/1.

[c] [2-hexanol]/[3-hexanol] = 0.7/1.

[d] [2-hexanone]/[3-hexanone] = 0.8/1.

[e] [2-heptanol]/3-heptanol]/[4-heptanol] = 0.8/2/1.

[f] [2-heptanone]/[3-heptanone]/[4-heptanone] = 1.4/1.6/1.

[g] [2-octanol]/[3-octanol]/[4-octanol] = 0.3/1/2.

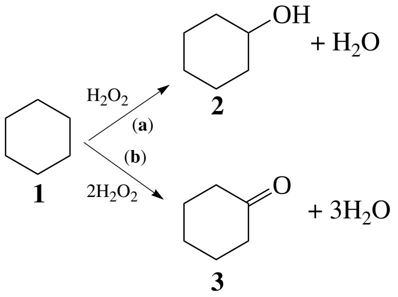
[h] [2-octanone]/[3-octanone]/[4-octanone] = 0.7/1.2/1.

[i] [2-nonanone]/[3-nonanone]/([4-nonanone] + [5-nonanone]) = 1.3/1/1.

provide an opportunity to study the main regularities of linear alkane oxidation using cyclohexane as an example. The number of cyclohexane oxidation products is considerably lower, and they are easier to analyze.

In the oxidation of cyclohexane (**1**) with hydrogen peroxide in the presence of vanadium(V) compounds in an AcOH solution at 20–50°C, only cyclohexanol (**2**) and cyclohexanone (**3**) were detected as the products (Scheme 4; Table 4).

Neither C–C bond cleavage products nor the products of skeletal isomerization of **1** were detected. The addition of 2-propanol (0.01–0.14 mol/l), which is more active in chain oxidation than cyclohexane, did not change the shape of the kinetic curves of the buildup of cyclohexanol and cyclohexanone. The inhibitors of free-radical chain reactions (*para*-benzoquinone, tetranitromethane, and tri-*tert*-butylphenol) in concentrations from 7×10^{-3} to 2×10^{-2} mol/l did not decrease the rates of buildup of cyclohexanol and cyclohexanone and their final concentrations. All these facts suggest a nonchain mechanism of cyclohexane oxidation.



Scheme 4. Reaction paths of cyclohexane oxidation.

As in the case of linear alkanes, the curves of buildup of compounds **2** and **3** in cyclohexane oxidation have no singular points and approach a limit related to H_2O_2 depletion. After the addition of a new portion of H_2O_2, the oxidation of cyclohexane recommenced at the previous rate.

Cyclohexanone was absent from the products of cyclohexanol oxidation in the $V^{(V)}/H_2O_2/AcOH$ system. In the simultaneous oxidation of cyclohexane and cyclohexanol in the test system, the buildup rates of compounds **2** and **3** were independent of the initial cyclohexanol concentration ($[\mathbf{2}]_0$). The limiting cyclohexanone concentration ($[\mathbf{3}]_\infty$), which was reached after

Table 3. Relative rate constants of alkane and cyclohexane oxidation ($k_A/k_{cyclohexane}$) in the $V^{(V)}/H_2O_2/AcOH$ system at 30°C

Alkane	$k_A/k_{cyclohexane}$
n-pentane	1.71 ± 0.05
n-heptane	0.88 ± 0.05
n-octane	0.64 ± 0.04
n-nonane	0.83 ± 0.05
n-decane	0.72 ± 0.04

the complete consumption of hydrogen peroxide, was also independent of $[\mathbf{2}]_0$. Thus, the formation of cyclohexanone from cyclohexanol, as well as the coupled oxidation of cyclohexane and cyclohexanol, can be excluded from consideration. All the data suggest that cyclohexanol and cyclohexanone are formed in parallel reactions (a) and (b) (Scheme 4) [24].

The initial rate of buildup of cyclohexanol was practically proportional to an increase in the concentration of vanadium(V) at constant initial concentrations of H_2O_2 and cyclohexane (Fig. 5). The rate of H_2O_2 decomposition remained unchanged regardless of the presence or absence of compound **1** and its oxidation products, all other factors being the same [24]. Therefore, the limiting concentration of an oxidation product, that is, the concentration reached after the complete consumption of H_2O_2, can characterize the rate of reaction. Table 4 summarizes the limiting conversions (x_∞) of cyclohexane and the limiting concentrations of the products. The data indicate that the rate of cyclohexanol buildup, which is characterized by $[\mathbf{2}]_\infty$, noticeably increased with $[H_2O_2]_0$ (Table 4, nos. 6, 7). In contrast to this, the limiting concentration of compound **2** depended only slightly on changes in the concentration of cyclohexane (Table 4, nos. 1, 2 and 3–5); this fact suggests that the order of reaction with respect to the concentration of cyclohexane is close to zero.

This may be due to the following reasons:

(1) a free-radical chain reaction mechanism, which includes quadratic termination;

(2) an inhibition of oxidation by reaction products;

(3) an inhibition of oxidation by a substrate because of the formation of its strong complex with the catalyst at a step that precedes the rate-limiting step;

(4) a steady-state concentration of an active oxidizing agent.

Assumption (1) can be rejected because of the absence of an induction period of the reaction. Moreover, the reaction is insensitive to traditional inhibitors and reactor material.

Assumption (2) is inconsistent with the results of experiments on the simultaneous oxidation of cyclohexane and cyclohexanol or cyclohexanone (see above). Assumption (3) can be rejected because there are no experimental data or theoretical considerations in support of the idea that cyclohexane can form strong complexes with vanadium compounds.

The formation of an active oxidizing agent at the rate-limiting step of the reaction (assumption (4)) seems most probable. The rate of deactivation of the active oxidizing agent, that is, its decomposition with the release of O_2, should be lower than the rate of its reaction with cyclohexane, or these rates should be close to each other in their order of magnitude. In terms of the mechanism of hydrogen peroxide conversion in

Table 4. Cyclohexane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system at 50°C

No.	$[V^{(V)}] \times 10^3$, mol/l	$[\mathbf{1}]_0$, mol/l	$[H_2O_2]_0$, mol/l	$[\mathbf{2}]_\infty \times 10^2$, mol/l	$[\mathbf{3}]_\infty \times 10^2$, mol/l	Conversion* of **1**, %
1	0.14	0.85	0.10	3.0	2.6	0.7
2	0.14	1.55	0.10	3.5	3.2	0.4
3	0.65	0.43	0.44	5.3	4.1	2.2
4	0.65	0.82	0.44	6.3	4.5	1.3
5	0.65	1.51	0.44	7.5	6.1	0.6
6	0.15	0.44	0.48	11	9.0	4.5
7	0.15	0.44	0.19	5.6	5.2	2.5
8	0.07	0.45	0.10	2.4	2.3	1.0
9	0.14	1.55	0.08	3.3	2.8	0.4
10	1.7	0.39	0.71	14	11	6.6
11	2.4	0.28	0.82	15	12	9.6
12	1.7	0.13	0.70	9.6	7.1	13

Note: **1** is cyclohexane, **2** is cyclohexanol, and **3** is cyclohexanone.
* Limiting conversion x_∞.

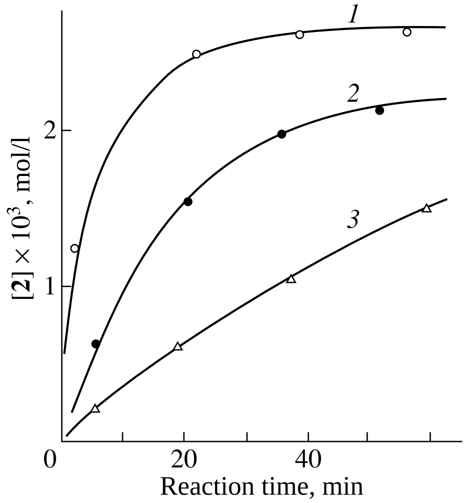


Fig. 5. Formation of cyclohexanol (*2*) in the oxidation of cyclohexane (*1*) in the $V^{(V)}/H_2O_2/AcOH$ system. 50°C; $[\mathbf{1}]_0 = 0.5$ mol/l; $[H_2O_2]_0 = 0.08$ mol/l; $[V^{(V)}]$ = (*1*) 3.8×10^{-4}, (*2*) 7×10^{-5}, or (3) 3×10^{-5} mol/l.

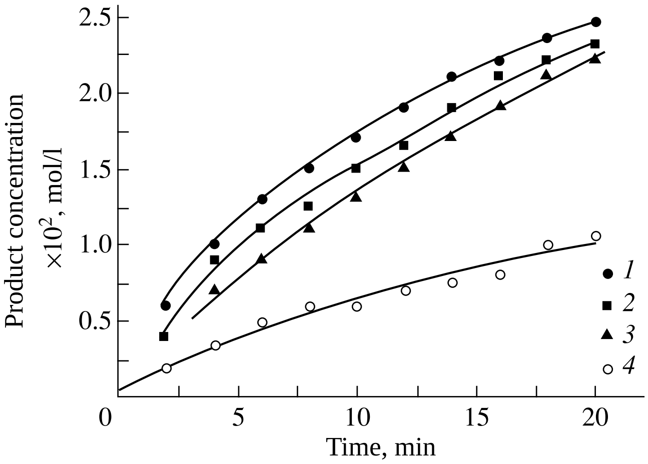


Fig. 6. Accumulation of (*1, 3*) cyclohexanol and (*2, 4*) cyclohexanone in the oxidation of cyclohexane (**1**) (*1, 2*) in the presence or (*3, 4*) in the absence of anthracene. [**1**] = 0.6 mol/l; [anthracene] = 0.1 mol/l; $[V^{(V)}] = 1.8 \times 10^{-4}$ mol/l; $[H_2O_2]_0 = 1.0$ mol/l; 30°C; $V^{(V)}/H_2O_2/AcOH$ system.

the test system (Scheme 1), only two intermediate complexes of vanadium are formed at two different slow steps:

(1) a vanadium complex with singlet dioxygen, which is responsible for the oxidation of unsaturated compounds;

(2) a vanadium complex with the trioxo ligand, which is the precursor of ozone.

It is well known that the vanadium complex with singlet dioxygen is responsible for the oxidation of 2-ethylanthracene. Let us assume that the same complex also reacts with alkanes. Then, for the simultaneous oxidation of cyclohexane and 2-ethylanthracene, we can write

$$-\frac{d[\mathrm{Sub}_1]}{dt} = \frac{k_1[\mathrm{Sub}_1]w_0}{k_{\mathrm{deact}} + k_1[\mathrm{Sub}_1] + k_2[\mathrm{Sub}_2]},$$

$$-\frac{d[\mathrm{Sub}_2]}{dt} = \frac{k_2[\mathrm{Sub}_2]w_0}{k_{\mathrm{deact}} + k_1[\mathrm{Sub}_1] + k_2[\mathrm{Sub}_2]},$$

where w_0 is the rate of formation of the vanadium complex with singlet dioxygen; $[\mathrm{Sub}_1]$ and $[\mathrm{Sub}_2]$ are the concentrations of cyclohexane and 2-ethylanthracene, respectively; k_{deact} is the rate constant of deactivation of an active intermediate; k_1 and k_2 are the rate constants of reactions of cyclohexane and 2-ethylanthracene with the active intermediate, respectively; $k_{\mathrm{deact}}/k_2 = 0.014$ mol/l [23].

A near-zero order of reaction with respect to the concentration of cyclohexane is observed if $k_1[\mathrm{Sub}_1] \geq k_{\mathrm{deact}}$. Then, in the simultaneous oxidation of cyclohexane and 2-ethylanthracene at $[\mathrm{Sub}_2] \geq 10^{-2}$ mol/l, either a decrease in the rate of cyclohexane oxidation (if $k_1[\mathrm{Sub}_1] \cong k_{\mathrm{deact}}$) or the termination of 2-ethylanthracene oxidation (if $k_1[\mathrm{Sub}_1] \gg k_{\mathrm{deact}}$) can occur.

We found experimentally that no considerable changes in the rate of buildup of cyclohexanol were observed in the presence of 2-ethylanthracene (0.1 mol/l). Similarly, the addition of cyclohexane (0.6 mol/l) had no effect on the rate of consumption of 2-ethylanthracene ($[\mathrm{Sub}_2]_0 = 2 \times 10^{-2}$ mol/l) (Fig. 6).

These facts allowed us to exclude the complex of vanadium with singlet dioxygen from the number of active intermediates responsible for alkane oxidation.

The experimental data suggest that an intermediate vanadium complex formed at another rate-limiting step is responsible for the consumption of alkanes in the $V^{(V)}/H_2O_2/AcOH$ system. This is the $V^{(V)}/(O_3)^{2-}$ complex with the trioxo ligand, which can oxidize an alkane to an alcohol and the corresponding ketone in parallel reactions.

Because CCl_4, which is a scavenger of C-centered free radicals [28], has no effect on the rate of buildup of an alcohol (Fig. 7) and radical chain oxidation of alkanes does not occur in the test system (see above), alkane hydroxylation can be considered as a purely molecular process of the insertion of one of the oxygen atoms of the trioxo ligand into a C–H bond of the hydrocarbon (Scheme 5, reaction path (I)). Note that the kinetic isotope effect (KIE) of cyclohexane hydroxylation with the complex with the trioxo ligand is close to unity (1.16 ± 0.07 [24]), whereas a much larger KIE (2.77 [13]) was obtained for cyclohexane hydroxylation with peroxo complexes. The small KIE is indicative of a minor elongation of the C–H bond in the transition state; that is, it is believed that in the reaction of the trioxo complex the electrophilicity of the oxygen atom inserted into the C–H bond is higher than that in the dipicolinate peroxo complex of vanadium [13].

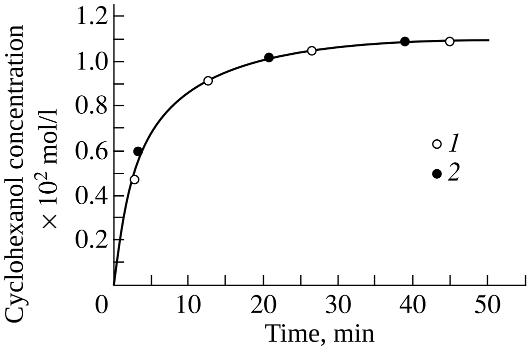


Fig. 7. Formation of cyclohexanol in the oxidation of cyclohexane (*1*) in the $V^{(V)}/H_2O_2/AcOH$ system (**1**) in the absence or (*2*) in the presence of CCl_4; 50°C; $[V^{(V)}] = 2 \times 10^{-4}$ mol/l; $[\mathbf{1}]_0 = 1.0$ mol/l; $[H_2O_2]_0 = 0.3$ mol/l; $[CCl_4]_0 = 1.2$ mol/l.

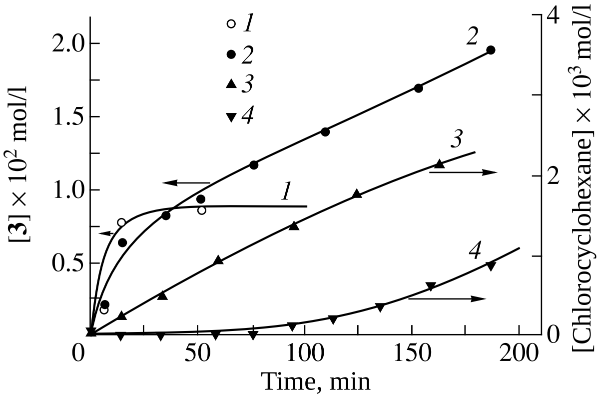


Fig. 8. Accumulation of cyclohexanone (*1*) in the absence of CCl_4 or (*2*) in the presence of CCl_4 (1.2 mol/l) and the accumulation of chlorocyclohexane in the presence of (*3*) CCl_4 (1.2 mol/l) or (*4*) CCl_4 (1.2 mol/l) and ionol (10^{-2} mol/l) in the oxidation of cyclohexane (**1**) in the $V^{(V)}/H_2O_2/AcOH$ system; 50°C; $[V^{(V)}] = 2 \times 10^{-4}$ mol/l; $[\mathbf{1}]_0 = 1.0$ mol/l; $[H_2O_2]_0 = 0.3$ mol/l.

The additives of CCl_4 insignificantly affected the initial rate of buildup of cyclohexanone; however, the following effects were observed in the presence of CCl_4 (Fig. 8):

(1) Cyclohexanone continued to accumulate after the exhaustion of hydrogen peroxide.

(2) The accumulation of chlorocyclohexane and hexachloroethane was observed.

(3) The addition of ionol inhibited the buildup of these products.

The above data suggest that, in the presence of CCl_4, along with the molecular mechanism of cyclohexane oxidation, the hydrocarbon can undergo chain oxidation. Carbon tetrachloride itself cannot initiate chain oxidation. It is likely that a chain initiator or chain carrier is formed as a result of CCl_4 reactions in the course of cyclohexane oxidation.

Thus, it is believed that a C-centered free radical is formed in the course of cyclohexane oxidation to cyclohexanone. This radical cannot carry out chain oxidation; however, it reacts with CCl_4 (a scavenger of C-centered free radicals) to form an effective chain carrier. The 1-hydroxy-1-cyclohexyl radical (Scheme 5, radical **C**), which is the product of the insertion of the $O^{+\bullet}$ species into a substrate C–H bond (Scheme 5, reaction path (II)), possesses these properties. Subsequently, this radical can react with oxygen to give the $HO_2^{\bullet}$ radical, which is inactive in cyclohexane oxidation, and cyclohexanone. The reaction of the 1-hydroxy-1-cyclohexyl radical with CCl_4 also results in the formation of cyclohexanone and, in addition, hydrogen chloride and the $CCl_3^{\bullet}$ radical, which can dimerize to hexachloroethane (hexachloroethane was detected in the oxidation products of **1**). The $CCl_3O_2^{\bullet}$ radical reacts with molecular O_2 to give $CCl_3O_2^{\bullet}$, which can carry out the chain oxidation of a hydrocarbon [28]. KIE (k_H/k_D) for the buildup of cyclohexanone in the test system is much higher than that for cyclohexanol and equal to 2.45 ± 0.09 [24]. This is consistent with the proposed mechanism, which includes the insertion of the oxygen radical cation into a C–H bond and the elimination of a proton at the same carbon atom (Scheme 5). It is likely that these processes occur synchronously. The reaction scheme proposed is consistent with all the experimental facts. The hypothesis of the participation of the oxygen radical cation ($O^{+\bullet}$) in oxidation reactions catalyzed by copper complexes was first proposed by Shilov [29].

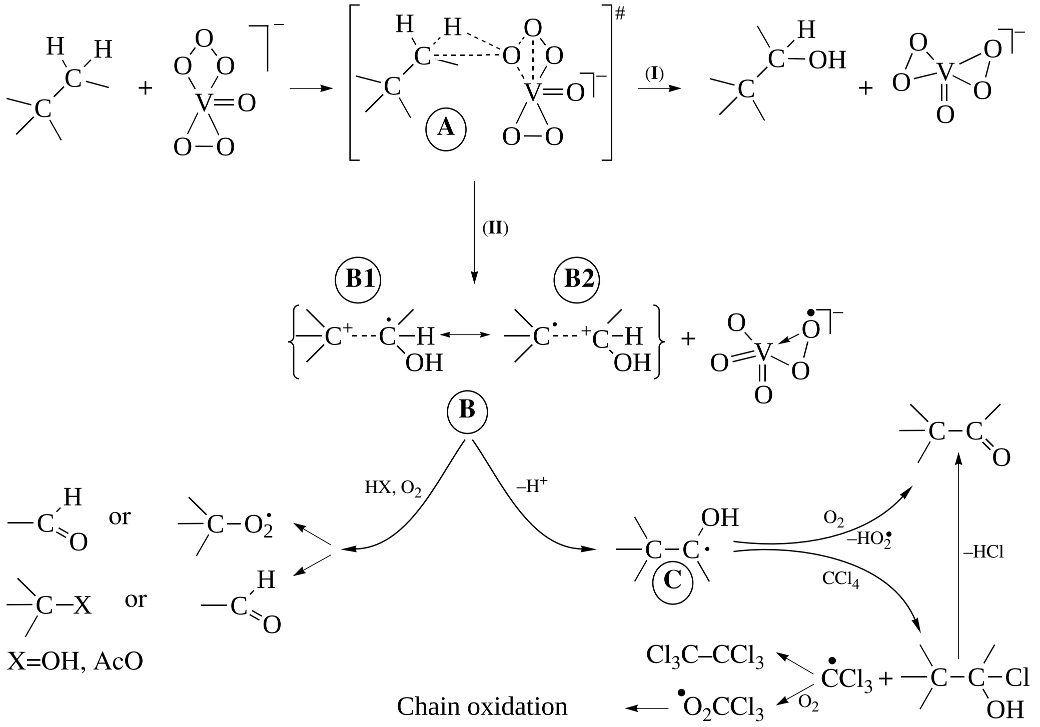
Oxidation of Branched Alkanes

Oxidation of 2,2-dimethylbutane. In the oxidation of 2,2-dimethylbutane in the $V^{(V)}/H_2O_2/AcOH$ system, in addition to the products of substrate oxidation at the methylene group (3,3-dimethyl-2-butanone (**4**) and 3,3-dimethyl-2-butanol (**5**)), primary alcohols (3,3-dimethyl-1-butanol (**6**) and 2,2-dimethyl-1-butanol (**7**)) were also detected, which are the products of hydroxylation at methyl groups. The appearance of the following alcohols among the reaction products seems unusual: 2-methyl-2-propanol (**8**), 2,2-dimethyl-1-propanol (**9**), and 2-methyl-2-butanol (**10**). The numbers of carbon atoms in these alcohols are lower than that in the parent substrate (Scheme 6).[5]

Oxidation of 2-methylpentane. In the oxidation of 2-methylpentane, we expected that the process would affect only the C–H bonds of methyl, methylene, and methyne groups. Indeed, the following products of this oxidation were detected in the reaction solutions:

---

[5] Oxidation products containing lower numbers of carbon atoms than that in the parent substrate were detected as alcohols and esters in the reaction mixture. However, for simplicity, henceforth, only the corresponding alcohols are shown in reaction schemes.



Scheme 5. Hypothetical mechanism of alkane oxidation in the presence of $V^{(V)}/H_2O_2/AcOH$.

4-methyl-1-pentanol (**11**), 2-methyl-1-pentanol (**12**), 2-methyl-3-pentanol (**13**), 2-methyl-2-pentanol (**14**), 4-methyl-2-pentanol (**15**), 2-methyl-3-pentanone (**16**), 4-methyl-2-pentanone (**17**), and 2-methylpentanal (**18**). In addition to these products, 2-pentanol (**19**) and 2-pentanone (**20**) were also detected; the carbon skeleton of these compounds is shorter than that in the parent substrate (Scheme 7).

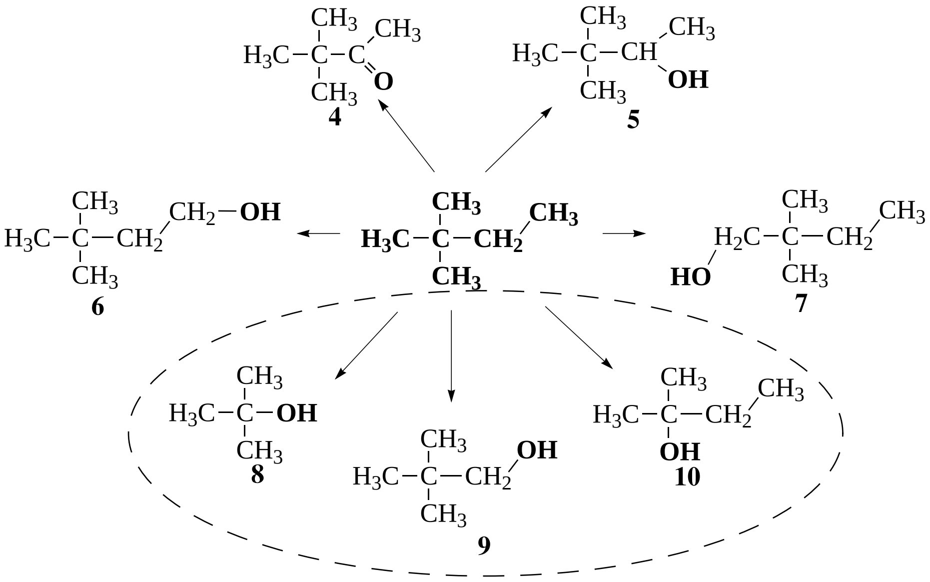
Oxidation of 3-methylpentane. The predominant products of 3-methylpentane oxidation in the test system are 3-methyl-2-pentanone (**21**) and 3-methyl-3-pentanol (**22**). Other hydrocarbon oxidation products were also detected, in which the carbon skeleton of the substrate was retained: 3-methyl-2-pentanol (**23**), 3-methyl-1-pentanol (**24**), 2-ethyl-1-butanol (**25**), and 3-methylpentanal (**26**). In addition to the oxidation products expected, the following alcohols, their esters, and ketones, whose carbon skeletons contain lower numbers of carbon atoms than that in the initial substrate, were identified by GC–MS: 3-pentanol (**27**), 3-pentanone (**28**), 2-butanone (**29**), 2-butanol (**30**), 2-butyl acetate and ethanol (**31**), and ethyl acetate (Scheme 8).

Oxidation of 2,3-dimethylbutane. Among the oxidation products of 2,3-dimethylbutanol, 2,3-dimethyl-2-butanol (**32**) was predominant. Other oxidation products, in which the carbon skeleton of the substrate was retained, were also detected in the reaction solutions: 2,3-dimethyl-1-butanol (**33**), 2,3-dimethylbutanal (**34**), and 2,3-dimethyl-2-butene (**35**). In addition to the above compounds, the following compounds with lower numbers of carbon atoms in the molecular skeleton than that in the parent substrate were also detected among the oxidation products of 2,3-dimethylbutane: 2-propanol (**36**), 3-methyl-2-butanol (**37**), and 3-methyl-2-butanone (**38**) (Scheme 9).

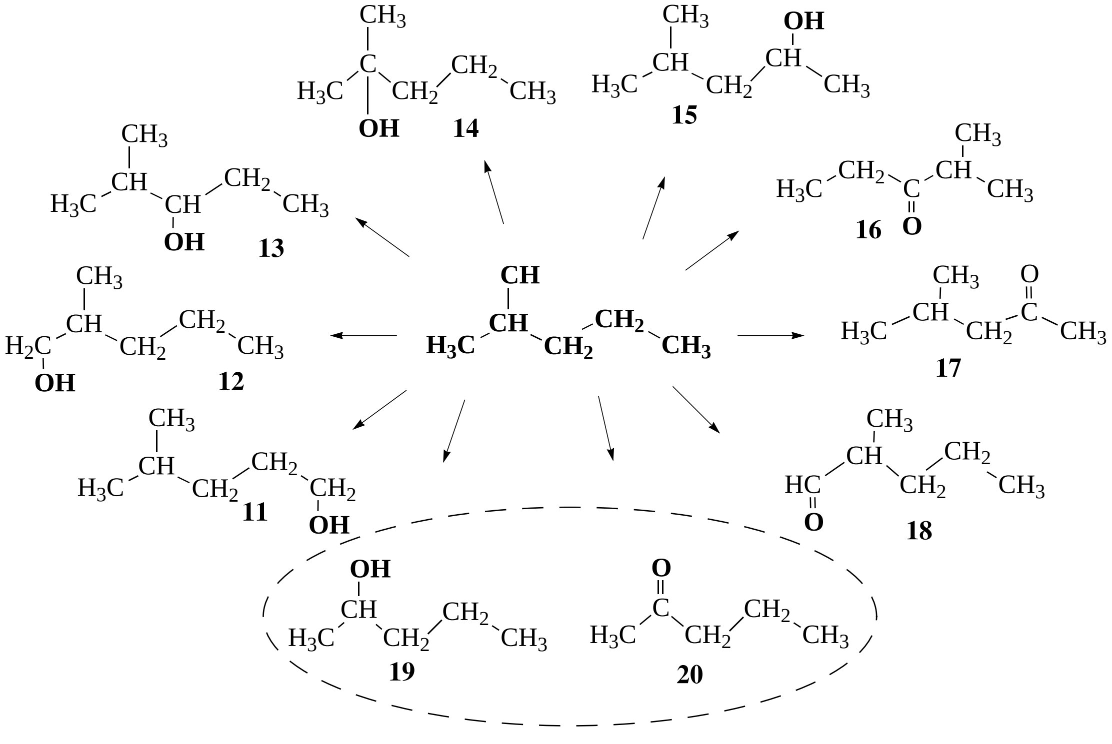
Oxidation of isooctane. The fullest information on the reactivity of various C–C bonds can be obtained from the oxidation of isooctane, in the molecule of which primary, secondary, tertiary, and quaternary carbon atoms occur simultaneously. Therefore, its oxidation products were studied in more detail than the oxidation products of other branched alkanes.

2,2,4-Trimethyl-3-pentanone (**39**, the main product), 2,2,4-trimethyl-3-pentanol (**40**), 2,2,4-trimethyl-1-pentanol (**41**), 2,4,4-trimethyl-1-pentanol (**42**), and 2,4,4-trimethyl-1-pentene (**43**), as well as compounds with shortened hydrocarbon chains (4,4-dimethyl-2-pentanol (**44**), 2,4-dimethyl-2-pentanol (**45**), 4,4-dimethyl-2-pentanone (**46**), 1,1-dimethylethanol (**47**), 2-methyl-1-propanol (**48**), 2-methyl-1-propyl acetate, 2,2-dimethyl-1-propanol (**49**), 2,2-dimethyl-1-propyl acetate, 4-methyl-2-pentanone (**50**), and 4-methylpentan-4-ol-2-one (**51**)) were detected by GC–MS in the reaction mixture of isooctane oxidation. A trace of 2-propanol was also detected (Scheme 10).

Free-radical chain reaction inhibitors, such as ionol and *para*-benzoquinone, have no effect on the product composition of isooctane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system. This makes it possible to



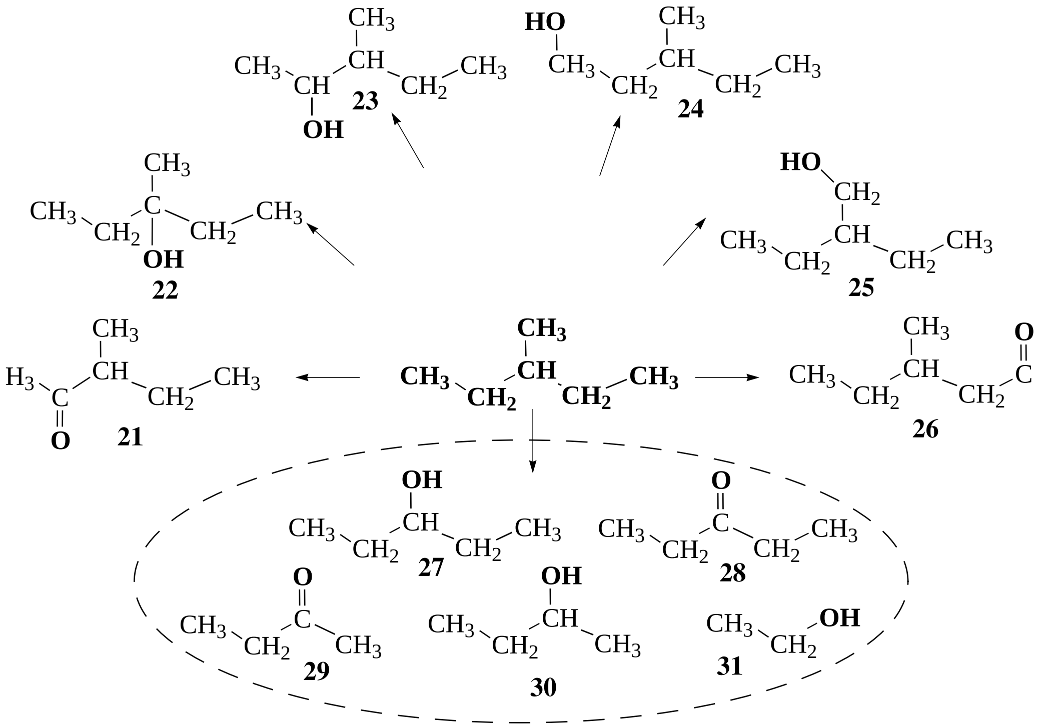
Scheme 6. Identified products of 2,2-dimethylbutane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.



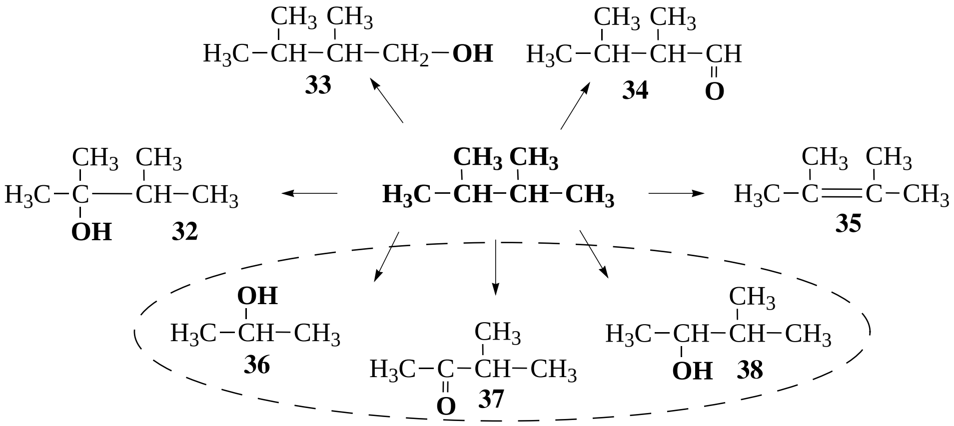
Scheme 7. Identified products of 2-methylpentane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.

exclude the chain oxidation of this substrate and the above hydrocarbons.

By analogy with the oxidation of cyclohexane and *n*-alkanes, which was described above, the expected products of isooctane conversion in the $V^{(V)}/H_2O_2/AcOH$ system would be 2,2,4-trimethyl-3-pentanone (**39**) and 2,2,4-trimethyl-3-pentanone (**40**), which result from the oxidation of the sole methylene group of isooctane. However, along with these compounds, the following products of methyl group hydroxylation were also observed: 2,2,4-trimethyl-1-pentanol (**41**) and 2,4,4-trimethyl-1-pentanol (**42**). Surprisingly, 2,2,4-trimethyl-2-pentanol (a product of hydroxylation at the tertiary carbon atom of isooctane), which is expected based on free-radical reaction schemes and schemes with the abstraction of the hydride

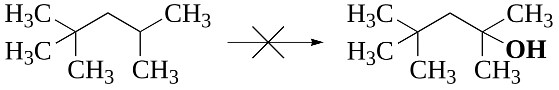


Scheme 8. Identified products of 3-methylpentane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.



Scheme 9. Identified products of 2,3-dimethylbutane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.

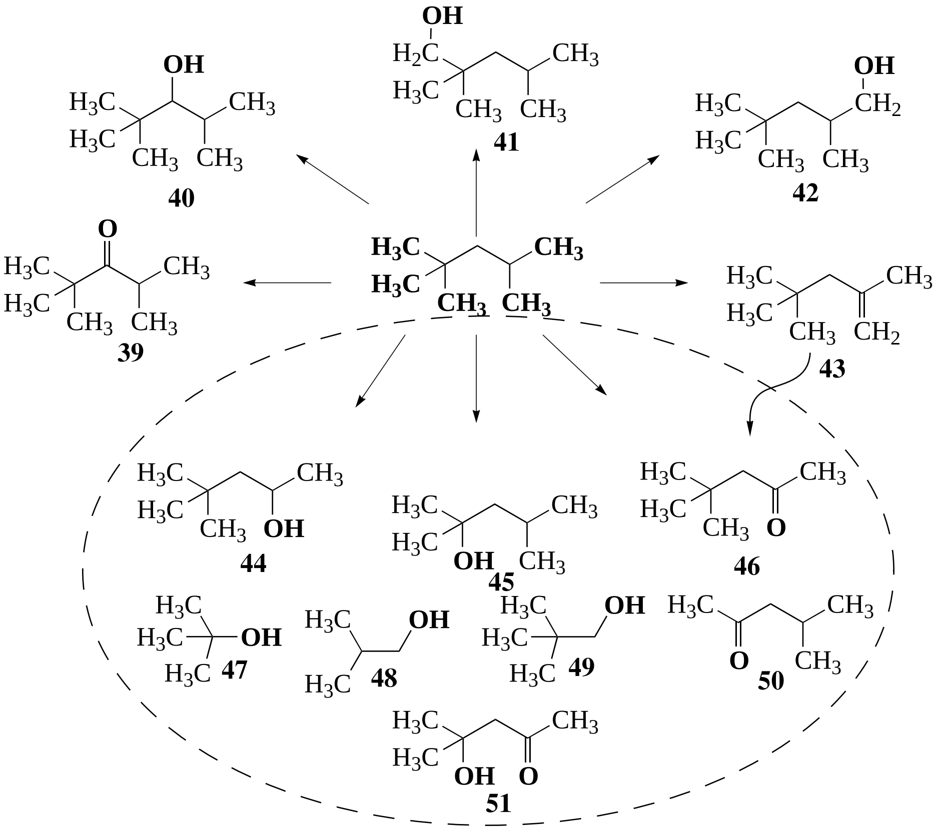
ion from the alkane, was not found in this reaction:



It is likely that this alcohol or the corresponding acetate gives 2,4,4-trimethyl-1-pentene (**43)**, which was detected in the reaction mixture, as a result of dehydration or AcOH elimination.

Oxidative dehydrogenation was observed in the reaction of cyclooctane in the GIF system (Fe(III) salt/TBHP) [30]. In this context, the formation of 4,4-dimethyl-2-pentanone (**46**) (Scheme 10) can be explained by the oxidative dehydrogenation of isooctane (more precisely, alkane hydroxylation followed by alcohol dehydration) and the oxidative cleavage of 2,4,4-trimethyl-1-pentene (**43**). It is well known that oxidative cleavage can occur in the $V^{(V)}/H_2O_2/AcOH$ system [20, 21].

Evidently, the formation of 4,4-dimethyl-2-pentanol (**44**) and 2,4-dimethyl-2-pentanol (**45**) in isooctane oxidation is indicative of C–C bond cleavage. This is the least expected route in the test reaction. The presence of C_4–C_7 hydrocarbon derivatives (**44**–**51**, Scheme 10) in the reaction products cannot be explained by the occurrence of corresponding impurities in the parent isooc-



Scheme 10. Identified products of isooctane oxidation in the $V^{(V)}/H_2O_2/AcOH$ system.

tane. The GLC analysis of the parent hydrocarbon demonstrated that the isooctane purity was higher than 99.8%, the concentration of 2,2-dimethylpentane and 2,4-dimethylpentane was no higher than 0.02%, and the concentration of C_4–C_6 hydrocarbons was lower than 0.01%. Thus, the formation of products **44**–**51** cannot be explained by oxidation of C_4–C_7 alkane admixtures in initial isooctane. We can conclude that alcohols and ketones with shortened carbon chains (1,1-dimethylethanol (**47**), 2-methyl-1-propanol (**48**), 2,2-dimethyl-1-propanol (**49**), 4-methyl-2-pentanone (**50**), 4-methylpentan-4-ol-2-one (**51**), and 2-propanol) are formed from isooctane in processes that result in C–C bond cleavage.[6]

In the test system, the oxidation of both linear and branched alkanes primarily occurs at the C–H bonds of the substrate with retention of the molecular carbon skeleton. In this case, primary C–H bonds are much less reactive than secondary and tertiary bonds, although difference between the activities of primary and secondary C–H bonds is less pronounced in the oxidation of branched alkanes. In both cases, the ketone content of the reaction products was higher than the concentration of corresponding alcohols.

Similar transformations were observed in the oxidation of alkanes with dioxygen catalyzed by Co(II)/Co(III) in a solution of CF_3COOH [31, 32].

Some distinctions between the oxidation of saturated branched-chain hydrocarbons and the reactions of linear alkanes should be noted:

(1) In the oxidation of linear alkanes, alcohols and ketones with carbon chains shortened compared to the chain of the parent substrate are not formed, whereas the concentration of shorter chain alcohols and ketones in the oxidation products of branched hydrocarbons is comparable with the amount of “normal” hydroxylation and ketonization products. In this case, oxidative degradation primarily occurs at the C_{tert}–C bond.

(2) Esters were detected only for alcohols with chains shortened compared to the carbon skeleton of the initial substrate, whereas esters were not detected for substrate hydroxylation products (the molecular carbon skeleton was retained).

(3) Primary alcohols and aldehydes were detected in the oxidation products of branched alkanes, whereas the terminal methyl groups of linear alkanes remained unaffected.

All these facts, as well as the regularities of alkane hydroxylation, can be explained in terms of the mechanism that involves a common transition state for all of

---

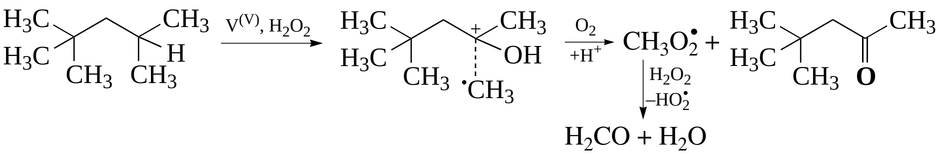
[6] 2-Propanol is fairly soluble in water. For this reason, in the course of sample preparation by extraction with diethyl ether, a considerable portion of 2-propanol remained in the water causing an underestimate of the apparent yield of this compound.

the alkane conversion routes (hydroxylation, ketonization, and oxidative degradation) (Scheme 5). As in the oxidation of cyclohexane, the vanadium(V) complex with the trioxo ligand (Scheme 5) is taken as the active oxidizing agent in these reactions. In activated complex **A**, a C–H bond of the alkane molecule is subjected to an electrophilic attack by an oxygen atom of the trioxo group. Depending on the mode of C–H bond vibrations in the attacked hydrocarbon fragment of the alkane molecule, the activated complex can decompose to form different products. In the case of antisymmetric valence vibrations of the H–C–H group (Scheme 5, reaction path (**I**)), the oxygen atom is inserted into a C–H bond, and an alcohol molecule and a diperoxo complex of vanadium are formed. In the case of symmetrical valence vibrations, it is likely that the oxygen radical cation is inserted into a C–H bond (reaction path (**II**)). In this case, a radical–cation pair (**B**) and a complex of the superoxide anion with $V^{(V)}$ are formed. As evidenced by EPR spectra, the latter species always occurred in the reaction solutions [6, 7]. Radical–cation pair **B**, in which a positive charge and an unpaired electron are mainly localized at different carbon atoms, can participate in the following reactions:

(1) Conversion into a radical **C** with the elimination of a proton and the subsequent oxidation to a carbonyl compound (it is not improbable that the radical is directly formed from transition state **A** as a result of a synchronous process: the insertion of the oxygen radical cation $O^{+\bullet}$ into a C–H bond and the elimination of a proton bound to the same carbon atom through another bond).

(2) Reaction with a nucleophilic species and molecular oxygen. In this case, the direction of the nucleophilic attack and, probably, the rate of the reaction depend on the predominant localization of a positive charge, whereas molecular oxygen abstracts a hydrogen atom from the carbon atom at which an unpaired electron is mainly localized. In this case, C–C bond cleavage takes place. Radical cation **B** can undergo the following two transformations: (1) If the contribution of structure **B1** is greater than that of **B2**, an alcohol or its ester and a carbonyl compound with a chain shortened compared to the substrate (an aldehyde or ketone at R = H or alkyl, respectively). (2) If the contribution of structure **B2** is greater than that of **B1**, a nucleophilic attack on the $^{+}C(OH)R$ group results in the same carbonyl compound. The free-radical fragment $CH_3^{\bullet}$ or $C_2H_5^{\bullet}$ gives a peroxy radical, which could in principle carry out chain oxidation; however, it is not an active initiator [28]. Indeed, we experimentally found that the addition of ionol, which is an inhibitor of free-radical chain reactions, did not change the composition and ratio of oxidation products.

The proposed reaction scheme explains almost completely the kinetics of the oxidative degradation of branched alkanes. The only disadvantage of this scheme is that we failed to detect low-molecular-weight aldehydes (formaldehyde, acetaldehyde, and propionaldehyde) in the oxidation products of 2-methylpentane and 3-methylpentane. However, the procedure used for the identification of mixture components cannot reliably identify low-molecular-weight aldehydes in such complex mixtures. At the same time, the appearance of all of the other oxidative degradation products, including difficult-to-predict compounds, is adequately explained in terms of the proposed mechanism. Thus, it is well known that alcohols in acetic acid solutions do not undergo esterification under the conditions of our experiments. However, alkyl acetates with shortened carbon chains, such as 2-butyl acetate and ethyl acetate, were found in the reaction mixture (Scheme 8). According to Scheme 5, these esters result from an attack of a nucleophile HX on the electrophilic center of a radical–cation pair at the site of positive charge localization (resonance structure **B1**). The products of C–C bond cleavage with the formation of a ketone appear unusual (Scheme 7, product **20**; Scheme 8, product **28**; Scheme 9, product **38**; and Scheme 10, product **46**). The mechanism of their formation can be represented as follows:



Oxidation of Linear Fatty Acid Methyl Esters

Other evidence of oxidative C–C bond cleavage catalyzed by the $V^{(V)}/H_2O_2/AcOH$ system was found in a study of the oxidation of unbranched FAMEs.

As in the case of alkanes, in the absence of a catalyst from a solution of $H_2O_2/AcOH$, FAME consumption was not observed for several hours. The reaction began only after the addition of a catalyst (~10^{-2} mol/l vanadium compound) to the reaction mixture. The decomposition of H_2O_2 was complete after ~1 h at 30°C. As in the oxidation of alkanes, the FAME amount consumed monotonically increased with initial H_2O_2 concentration ($[H_2O_2]_0$) (Fig. 9). A more than tenfold molar excess of H_2O_2 was required for reaching a limiting FAME conversion (x_∞ = 90%).[7]

---

[7] The limiting substrate conversion was determined after the complete consumption of H_2O_2.

According to our data, the relative reactivity of FAMEs increases with the number of carbon atoms in the hydrocarbon skeleton (Fig. 9). The longer the carbon chain of the molecule, the smaller the excess of H_2O_2 required for reaching a fixed degree of substrate conversion.[8]

We found that not only the hydrocarbon chains of aliphatic FAMES are shortened in the course of reaction but also hydroxyl and keto groups are actively formed in this case (Table 5). For example, three isomers of hydroxyheptanoic acid, three isomers of hydroxyhexanoic acid, three isomers of hydroxypentanoic acid, two isomers of hydroxybutanoic acid, and glycolic acid were formed in the oxidation of methyl octanoate along with products with the same hydrocarbon-chain length as that in the parent FAME.

The good water solubility of reaction products and their trend to condensation reactions present problems for the quantitative analysis of the reaction mixture. However, based on the chromatographic peak intensities, we can conclude that glycolic acid or its ester predominates over the oxidation products.

The oxidation of acetic acid (i.e., the solvent) could be a source of glycolic acid in the test system. To reveal the routes of glycolic acid formation, we studied the oxidation of methyl stearate in CD_3COOD. In the chromatogram of the oxidation products treated with BSTFA, a signal was detected with the mass spectrum that corresponds to the unlabeled trimethylsilyl ester of glycolic acid $(CH_3)_3SiOCH_2COOSi(CH_3)_3$ (Fig. 10). The absence of D atoms from the CH_2 group excludes the possibility of glycolic acid formation from the solvent. Moreover, glycolic acid was not detected in the oxidation products of methyl isobutanoate because the oxidative degradation of methyl isobutanoate in principle cannot result in the formation of glycolic acid. We can conclude that the formation of glycolic acid is indicative of the oxidative degradation of FAMEs in the test system.

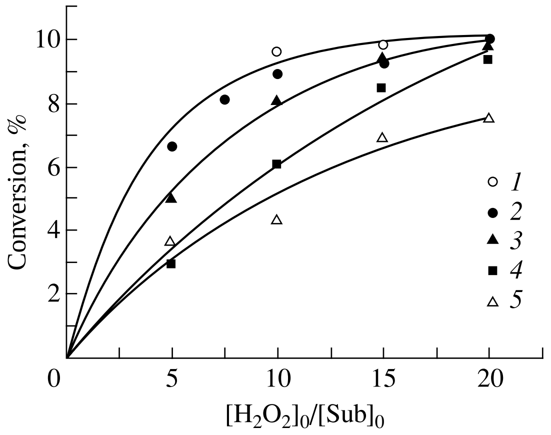


Fig. 9. Limiting FAME conversion as a function of $[H_2O_2]_0/[Sub]_0$ in the oxidation of the following compounds in the $V^{(V)}/H_2O_2/AcOH$ system: (*1*) methyl stearate, (*2*) methyl stearate with the addition of 2-ethylanthracene (~10^{-2} mol/l), (*3*) methyl caprylate, (*4*) methyl butyrate, and (*5*) methyl propionate.

The presence of other identified compounds with chains shorter than that in the parent FAME in the products also provides support for the conclusion on the oxidative degradation of FAMEs:

$$CH_3(CH_2)_nCOOMe \xrightarrow{H_2O_2,\ AcOH,\ V^{(V)}} HO{-}CH_2(CH_2)_nCOOH$$
$$+\ HO{-}CH_2(CH_2)_{n-1}COOH + \ldots + \mathbf{HOCH_2COOH.}$$

We found experimentally that the composition and distribution of the reaction products and the conversion of FAMEs remained unchanged in the presence of ionol, which is an effective scavenger of O-centered radicals. Analogously, the addition of 2-ethylanthracene had no effect, in particular, on the oxidation of methyl stearate. These facts demonstrate that a free-radical chain reaction mechanism does not take place in the case under consideration.

It would be expected that the electronegative group CH_3OOC^- in the FAME molecule would decrease the reactivity of the aliphatic hydrocarbon chain. However, the actual rate of FAME oxidation insignificantly differed from the rates of oxidation of cyclohexane and aliphatic alkanes. As well as alkanes, the FAME molecule oxidized with the formation of the corresponding hydroxy and keto acids and their esters.

The above facts suggest a similarity between the mechanism of the oxidative degradation of alkanes, which is presented in Scheme 5, and the mechanism of FAME oxidation. In the case of alkanes, which cannot coordinate to the $V^{(V)}$ atom, an attack occurs at the most reactive C–H bond of the substrate. However, in contrast to alkanes, FAMEs can coordinate to the $V^{(V)}$ atom through the ester group, and the insertion of the oxygen radical cation into a C–H bond occurs within the inner sphere. It is likely that the ability of the FAME molecule to form a complex with vanadium(V) through the coordination of the carboxyl O atom affects both the rate and the selectivity of the reaction. This should be

---

[8] The test reaction includes the oxidative cleavage of the hydrocarbon chain of a methyl ester (see below). Therefore, the number of moles of H_2O_2 required for the oxidation of 1 mol of FAMEs should increase with the length of the hydrocarbon chain. This would result in underestimated rather than overestimated reactivities of long-chain FAMEs; that is, the experimental data obtained are undoubtedly reliable.

Table 5. Products of FAME oxidation in the $V^{(V)}/H_2O_2$/AcOH system at 30°C

FAME	Oxidation products and their concentrations on a glycolic acid basis*	
cyclo-$C_6H_{11}COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_3H_6COOH 0.35,
		$HOC_6H_{10}COOH$ 9.30
EtCOOMe	Hydroxy acids:	$HOCH_2COOH$ 1.0,
		HOC_2H_4COOH (2) 0.23
n-PrCOOMe	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_2H_4COOH (2) 0.15,
		HOC_3H_6COOH (2) 0.24
iso-PrCOOMe	Hydroxy acids:	HOC_2H_4COOH (1) 1.00,**
		HOC_3H_6COOH (1) 2.30
iso-$PrCH_2COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_4H_8COOH (1) 0.29
$Me(CH_2)_5COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_3H_6COOH (3) 4.75,
		HOC_4H_8COOH (1) 6.65,
		$HOC_5H_{10}COOH$ (1) 4.67,
		$HOC_6H_{12}COOH$ (4) 12.90
	Dicarboxylic acid:	$HOOCC_5H_{10}COOH$ (1) 2.00
$Me(CH_2)_6COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_3H_6COOH (3) 1.13,
		HOC_4H_8COOH (1) 0.65,
		$HOC_5H_{10}COOH$ (1) 1.40,
		$HOC_6H_{12}COOH$ (1) 0.85,
		$HOC_7H_{14}COOH$ (5) 6.65,
	Keto acid:	$CH_3(CH_2)_nC(O)(CH_2)_{5-n}COOH$ (2) 2.77
$Me(CH_2)_7COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_3H_6COOH (1) 0.24,
		HOC_4H_8COOH (1) 0.94,
		$HOC_5H_{10}COOH$ (1) 1.08,
		$HOC_8H_{16}COOH$ (3) 6.78,
	Keto acid:	$CH_3(CH_2)_nC(O)(CH_2)_{6-n}COOH$ (3) 5.21,
	Dicarboxylic acid:	$(COOH)_2$ 0.12
$Me(CH_2)_{14}COOMe$	Hydroxy acids:	$HOCH_2COOH$ 1.00,
		HOC_2H_4COOH (2) 0.38,
		HOC_3H_6COOH (1) 0.22,
		$HOC_5H_{10}COOH$ (1) 0.08,
		$HOC_6H_{12}COOH$ (1) 0.09,
		$HOC_7H_{14}COOH$ (1) 0.26,
		$HOC_8H_{16}COOH$ (1) 0.11,
	Dicarboxylic acids:	$HOOCC_5H_{10}COOH$ (1) 0.18,
		$HOOCC_7H_{14}COOH$ (1) 0.17
$Me(CH_2)_{16}COOMe$	Hydroxy acid:	$HOCH_2COOH$ 1.00

* After extraction with chloroform, the reaction mixture was treated with BSTFA, and all of the products were analyzed and identified as trimethylsilyl derivatives; for example, $HOCH_2COOH$ was identified as $(CH_3)_3SiOCH_2COOSi(CH_3)_3$. The number of isomers found is given in parentheses.

** $HOCH_2COOH$ was not detected.

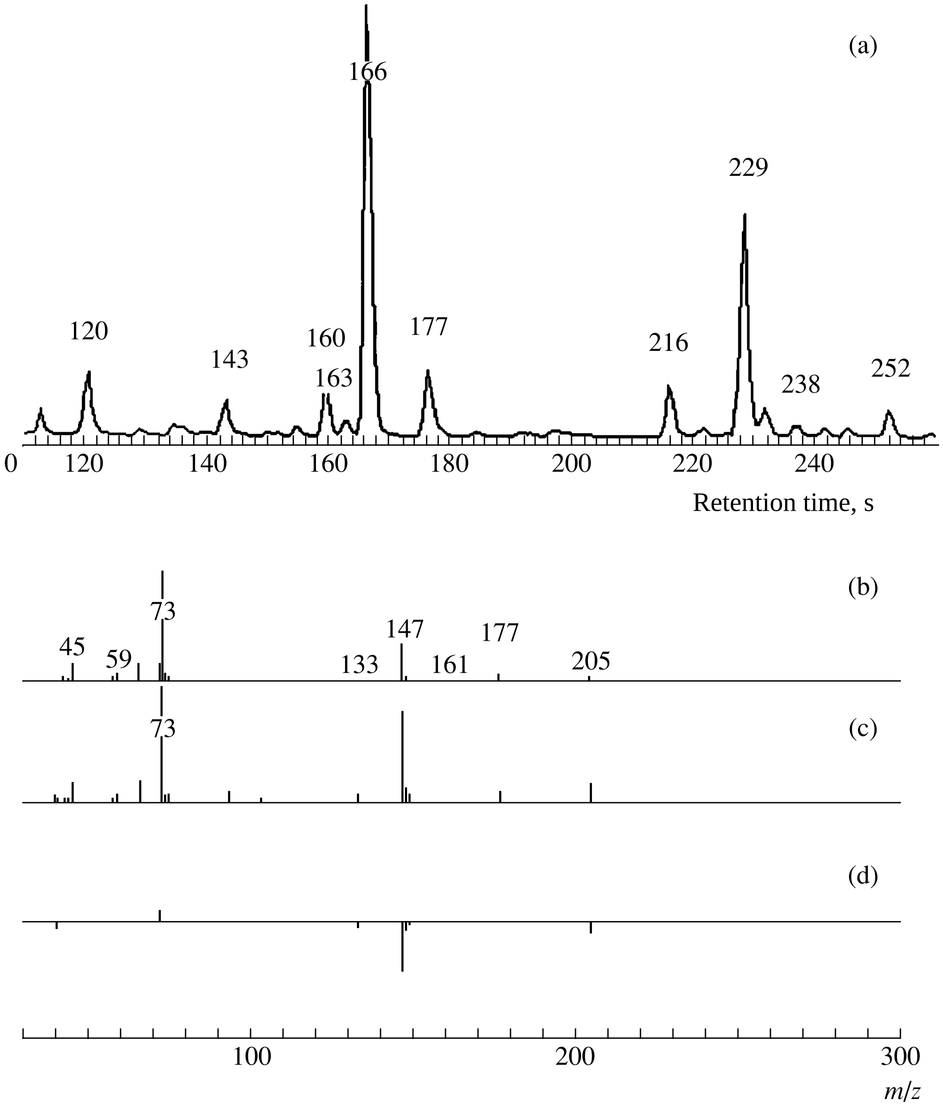


Fig. 10. Oxidation of methyl pelargonate in a CD_3COOD solution (30°C; $[V^{(V)}] = 4 \times 10^{-3}$ mol/l; $[Sub]_0 = 0.1$ mol/l; $[H_2O_2]_0 = 1$ mol/l): (a) chromatogram of the reaction mixture after treatment with BSTFA; (b) mass spectrum corresponding to the peak with a retention time of 166 s; (c) library spectrum of the trimethylsilyl ester of (trimethylsilyl)hydroxyacetic acid; and (d) difference between mass spectra (a) and (b).

taken into account in explaining the unexpectedly easy cleavage of the C–C bond in FAME oxidation. In this case, the direction of attack depends on the geometry of the intermediate complex of an active oxidizing agent and a substrate rather than the reactivity of a bond.

Oxidation of Molecular Nitrogen

A detailed analysis of the oxidation of cyclohexane led us to the conclusion that both of the products (cyclohexanol and cyclohexanone) result from the interaction of the alkane with the same slowly formed vanadium(V) intermediate, which is capable of transferring either the oxygen atom (two-electron oxidation) or the oxygen radical cation $(\mathrm{O}^{+\bullet})$ to the substrate (three-electron oxidation) [24, 29]. The entire variety of oxidation processes with the participation of the other test substrates (FAMEs and both branched and linear alkanes) can also be explained in terms of this hypothesis. Both of the species ($\mathrm{O}^{+\bullet}$ and the $O(^1P)$ atom) transferred to the substrate in the activated complex are strong acids (in terms of the Usanovich theory [33, 34]). We expected that these species could react even with weak bases such as molecular nitrogen. Indeed, we found experimentally that in the test system N_2 was converted into N_2O under very mild conditions (1 atm; 0–20°C):

$$N_2 + H_2O_2 \longrightarrow N_2O + H_2O.$$

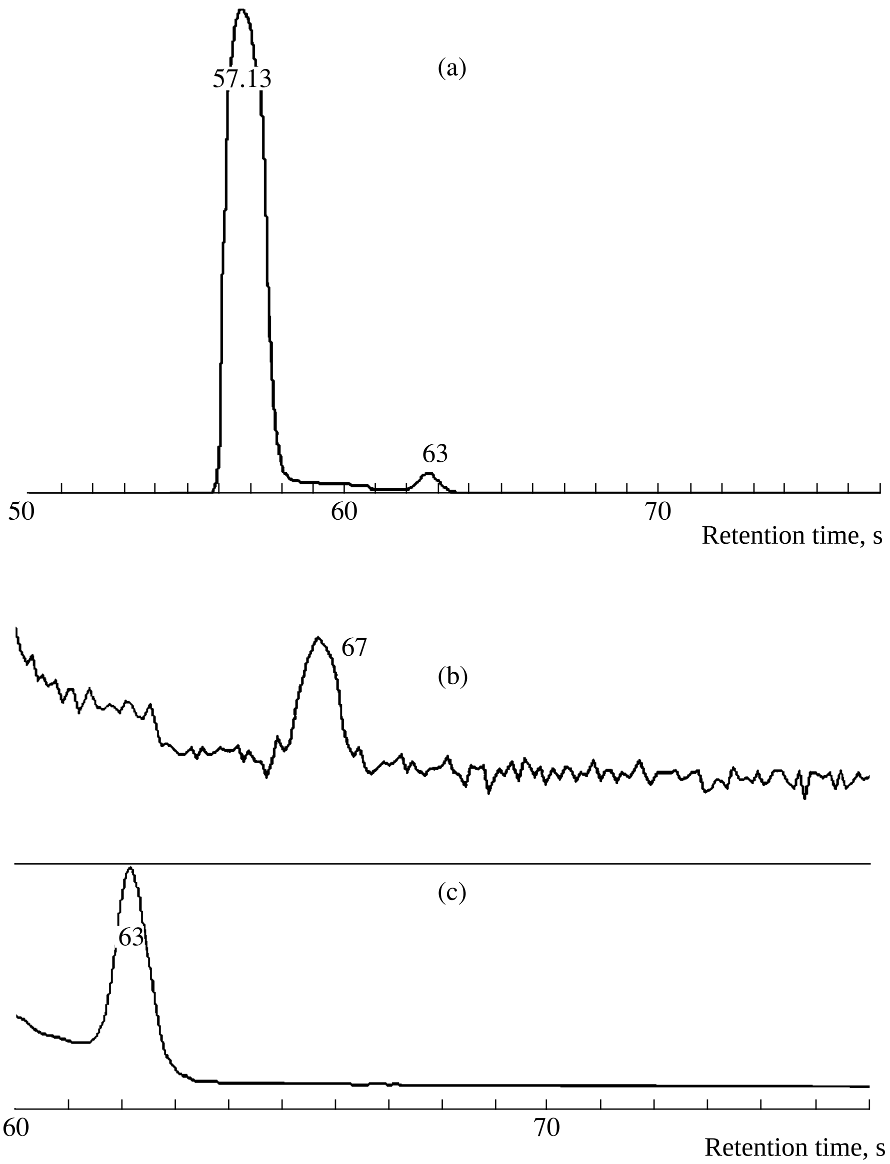


Fig. 11. Chromatograms of the gaseous products of N_2 oxidation in the $V^{(V)}/H_2O_2/CF_3COOH$ system: (a) total ion current chromatogram; (b) fragmentogram for $m/z = 30$; and (c) a portion of the total ion current chromatogram.

Note that the oxidation of molecular nitrogen to N_2O or NO with molecular dioxygen in the ground $^3O_2(^3\Sigma_g)$ and excited $^1O_2(^1\Delta_g)$ states under near-standard conditions is thermodynamically impossible.

The reaction of molecular nitrogen with ozone is allowed [35]:

$$N_{2(g)} + O_{3(g)} = N_2O_{(g)} + {}^3O_{2(g)},$$
$$\Delta G^{\circ}_{298} = -58.6 \text{ kJ/mol}.$$

However, this reaction is unknown, probably, because of the absence of an effective mechanism for oxygen-atom transfer from ozone to the substrate.

The oxidation of molecular nitrogen with hydrogen peroxide is also not forbidden thermodynamically:

$$2H_2O_{2(l)} + N_{2(g)} = 2NO_{(g)} + 2H_2O_{(l)},$$
$$\Delta G^{\circ}_{298} = -58.3 \text{ kJ/mol};$$

$$H_2O_{2(l)} + N_{2(g)} = N_2O_{(g)} + H_2O_{(l)},$$
$$\Delta G^{\circ}_{298} = -13.1 \text{ kJ/mol};$$

$$3H_2O_{2(l)} + N_{2(g)} = N_2O_{(g)} + 3H_2O_{(l)} + {}^3O_{2(g)},$$
$$\Delta G^{\circ}_{298} = -185.5 \text{ kJ/mol}.$$

The chromatogram of gaseous reaction products of N_2 oxidation with hydrogen peroxide in the presence of

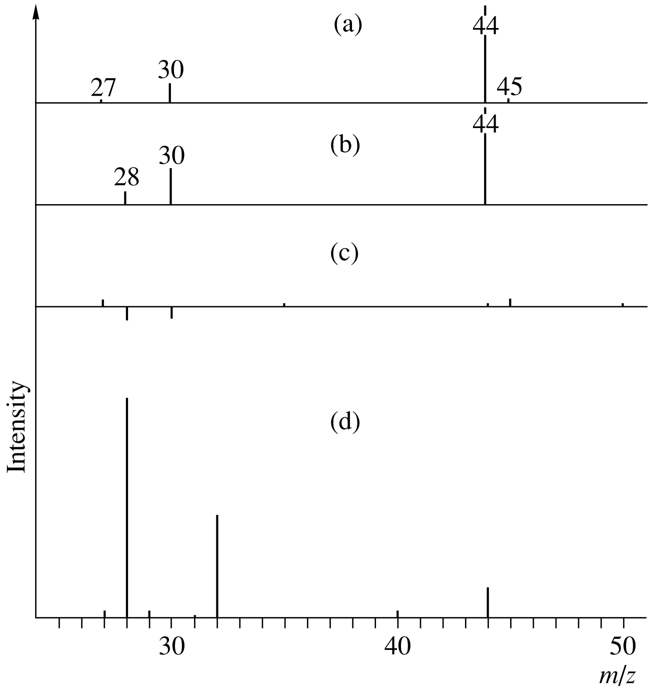


Fig. 12. Oxidation of molecular nitrogen in the $V^{(V)}/H_2O_2/CF_3COOH$ system: (a) mass spectrum of the component with a retention time of 67 s in the chromatogram of the gaseous products of N_2 oxidation (Fig. 11); (b) library electron-impact (70 eV) mass spectrum of nitrogen(I) oxide; (c) difference between mass spectra (a) and (b); and (d) baseline mass spectrum in the neighborhood of the chromatographic peak of N_2O.

$V^{(V)}$ in a CF_3COOH solution (Fig. 11a) exhibits, along with the unresolved chromatographic peaks of N_2 and O_2 (retention time of 57 s) and a peak due to CO_2 (retention time of 63 s), a low-intensity peak (Fig. 11c), which was detected in a fragmentogram recorded at $m/z = 30$ (Fig. 11b).

The mass spectrum of the component that corresponds to this chromatographic signal obtained by the subtraction of the averaged background before and after the chromatographic peak contains two signals of ions with $m/z = 44$ and 30, whose intensities are much higher than the other intensities (Fig. 12a). The experimental mass spectrum of the unknown component practically coincides with the published spectrum of N_2O (Fig. 12b), as evidenced by the difference between the mass spectra (Fig. 12c). The signal with $m/z = 28$ was absent from the experimental spectrum because it is difficult to correctly subtract the intense signals of background ions (Fig. 12d) from the spectrum of the eluted component whose concentration is extremely low.

Note that the chromatograms of samples of the gaseous nitrogen used in the experiments, as well as the chromatograms of the gaseous products of hydrogen peroxide decomposition in the $VO(acac)_2/CF_3COOH$ system in an atmosphere of helium, did not exhibit peaks similar in the retention time and in the shape of the spectrum to the chromatographic signal detected in nitrogen oxidation products.

The experimental data indicate that molecular nitrogen underwent oxidation in the $V^{(V)}H_2O_2/CF_3COOH$ catalytic system with the formation of N_2O.[9] Because nitrous oxide was not detected in the absence of a catalyst and hydrogen peroxide is stable, it is believed that a vanadium complex that oxidizes molecular nitrogen is formed by the interaction of $H_2O_2$with the catalyst.

The reaction found is the first example of the involvement of molecular nitrogen in catalytic hydroperoxide oxidation reactions.

CONCLUSIONS

In this work, an extended range of substrates allowed us to find a number of novel phenomena in the chemistry of peroxide oxidation. Thus, we observed for the first time the reactions of branched alkanes and the methyl esters of saturated linear long-chain carboxylic acids with carbon–carbon bond cleavage. The involvement of terminal methyl groups in oxidation is also unusual for this area of chemistry. Before this study, phenomena of this kind were observed in neither polar nor free-radical oxidation. The appearance of esters as hydroperoxide oxidation products seems to be an equally novel and unusual phenomenon.

The study demonstrated that, in the reaction of hydrogen peroxide with vanadium complexes, active intermediates are formed that can react with substrates that are difficult to oxidize with oxygen for thermodynamic reasons or because of a high activation barrier. Of course, the reaction schemes proposed are hypothetical. However, these mechanisms are consistent with the experimental facts observed, and they can serve as a basis for the design of further experiments.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 99-03-33248), the Federal Program of the Support for Leading Scientific Schools (grant no. 00-15-97429) and the Program “Fundamentals of Energochemical Technologies” of the Russian Academy of Sciences.

REFERENCES

1. Fenton, H.J., *J. Chem. Soc.*, 1894, vol. 65, p. 899.
2. Sheldon, R.A. and Kochi, J.K., *Metal-Catalyzed Oxidations of Organic Compounds*, New York: Academic, 1981, chapter 9.
3. Edwards, J.O., *Peroxide Reaction Mechanisms*, Edwards, J.O., Ed., New York: Wiley, 1962, p. 67.

---

[9] The procedure used in this work for the detection of products did not allow us to find other conceivable N_2 oxidation products: NO, NO_2, and HNO_3.

4. Edwards, J.O. and Curci, R., *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Strukul, G., Ed., Dordrecht: Kluwer Academic, 1992.
5. Syrkin, Ya.K. and Moiseev, I.I., *Usp. Khim.*, 1960, vol. 29, no. 4, p. 425.
6. Makarov, A.P., Gekhman, A.E., Nekipelov, V.M., Talzi, E.P., Polotnyuk, O.Ya., Zamaraev, K.I., and Moiseev, I.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 7, p. 1914.
7. Gekhman, A.E., Makarov, A.P., Nekipelov, V.M., Talzi, E.P., Polotnyuk, O.Ya., Zamaraev, K.I., and Moiseev, I.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 8, p. 1686.
8. Moiseeva, N.I., Gekhman, A.E., and Moiseev, I.I., *Gazz. Chim. Ital.*, 1992, vol. 122, p. 187.
9. Moiseeva, N.I., Gekhman, A.E., and Moiseev, I.I., *J. Mol. Catal., A: Chem.*, 1997, vol. 117, p. 39.
10. Moiseev, I.I., *Chemistry for the 21st Century*, Murahashi, S.-I. and Davies, S.G., Eds., Oxford: Blackwell Science, 1999, p. 343.
11. Moiseeva, N.I., Gekhman, A.E., Minin, V.V., Larin, G.E., Bashtanov, M.E., Krasnovskii, A.A., and Moiseev, I.I., *Kinet. Katal.*, 2000, vol. 41, no. 2, p. 191.
12. Makarov, A.P., Gekhman, A.E., Polotnyuk, O.Ya., and Moiseev, I.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 4, p. 765.
13. Mimoun, H., Saissine, L., Daire, E., Rostel, M., Fisher, J., and Weiss, R., *J. Am. Chem. Soc.*, 1983, vol. 105, p. 3101.
14. Begin, D., Einstein, F., and Field, S., *Inorg. Chem.*, 1975, vol. 14, p. 1785.
15. Szentivanyi, H. and Stomberg, R., *Acta Chem. Scand.*, 1983, vol. 37, p. 553.
16. Stomberg, R., *Acta Chem. Scand.*, 1984, vol. 38, p. 223.
17. Chaudhuri, M.K. and Ghosh, S.K., *Inorg. Chem.*, 1984, vol. 23, p. 534.
18. Fergusson, J.E. and Wilkins, C.J., *J. Chem. Soc.*, 1962, p. 2136.
19. Vol'nov, I.I., *Peroksokompleksy vanadiya, niobiya, tantala* (Peroxo Complexes of Vanadium, Niobium, and Tantalum), Moscow: Nauka, 1987.
20. Gekhman, A.E., Stolarov, I.P., Moiseeva, N.I., Rubaijlo, V.L., Vargaftik, M.N., and Moiseev, I.I., *Inorg. Chim. Acta*, 1998, vols. 275–276, p. 453.
21. Gekhman, A.E., Moiseeva, N.I., and Moiseev, I.I., *Dokl. Ross. Akad. Nauk*, 1996, vol. 349, no. 3, p. 53.
22. Gekhman, A.E., Amelichkina, G.E., Moiseeva, N.I., Vargaftik, M.N., and Moiseev, I.I., *J. Mol. Catal., A: Chem.*, 2000, vol. 162, p. 111.
23. Gekhman, A.E., Amelichkina, G.E., Moiseeva, N.I., Vargaftik, M.N., and Moiseev, I.I., *Kinet. Katal.*, 2001, vol. 42, no. 4, p. 549.
24. Moiseev, I.I., Shishkin, D.I., and Gekhman, A.E., *New J. Chem.*, 1989, vol. 13, nos. 10–11, p. 683.
25. Tietze, L.F. and Eicher, T., *Reactionen und Synthesen im Organisch-Chemischen Praktikum und Forschungslaboratorium*, Stuttgart: George Thieme, 1991.
26. Lubeck, A.J. and Sutton, D.L., *J. High Resolut. Chromatogr.*, 1983, no. 3, p. 328.
27. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1974.
28. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Reactions of Liquid-Phase Oxidation of Hydrocarbons), Moscow: Nauka, 1965.
29. Shilov, A.E., *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Dordrecht: Reidel, 1984.
30. Barton, D.H.R., Bévière, S.D., Chavasiri, W., Doller, D., and Hu, B., *Tetrahedron Lett.*, 1992, vol. 33, no. 38, p. 5473.
31. Vargaftik, M.N., Stolarov, I.P., and Moiseev, I.I., *J. Chem. Soc., Chem. Commun.*, 1990, p. 1049.
32. Stolarov, I.P., Vargaftik, M.N., Shishkin, D.I., and Moiseev, I.I., *J. Chem. Soc., Chem. Commun.*, 1991, p. 938.
33. Shatenshtein, A.I., *Teoriya kislot i osnovanii* (Theory of Acids and Bases), Moscow: Goskhimidat, 1949, p. 246.
34. Usanovich, M.I., *Issledovaniya v oblasti teorii rastvorov i teorii kislot i osnovanii* (Studies in the Theory of Solutions and the Theory of Acids and Bases), Alma-Ata: Nauka, 1970, p. 179.
35. *Termodinamicheskie svoistva individual'nykh veshchestv* (Thermodynamic Properties of Individual Substances), Glushko, V.P., Ed., Moscow: Akad. Nauk SSSR, 1962, vol. 2.