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CHEMISTRY

This paper is dedicated to Prof. Brian James (University of British Columbia, Canada) in recognition of his outstanding contribution to homogeneous catalysis and inorganic chemistry

C–C Bond Cleavage in Oxidation of Aliphatic Hydrocarbons under Mild Conditions in the V^V/H_2O_2/AcOH System

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The oxidation of alkanes by H_2O_2 in all available Fenton systems for hydroperoxide activation (Fe^{II}/Fe^{III}, V^{IV}/V^{V}, Cr^{V}/Cr^{VI}, Co^{II}/Co^{III}, etc.) results in alcohols and ketones [1–3]. In this paper, we report on the oxidation of alkanes (using isooctane as an example) and methyl esters of fatty carboxylic acids accompanied by the cleavage of a $>$C–C$<$ bond between the atoms bearing no functional groups.

The V^V/H_2O_2/AcOH system is capable of oxidizing different substrates such as cyclohexane, substituted alkenes, and anthracenes [4–10]. Parallel oxidation pathways of cyclohexane yields cyclohexanol and cyclohexanone, and a $>$C–C$<$ bond therewith remains intact [8]. Cyclohexane is oxidized more readily than acyclic hydrocarbons [1]; thus, it might be expected that the oxidation of alkanes in the system under consideration either does not take place or proceeds without $>$C–C$<$ bond cleavage.

In the absence of a catalyst, alkanes and methyl esters of higher fatty acids are stable to H_2O_2 solutions in acetic acid at 30–50°C over a period of 3–5 h. Introducing 10^{-2} M of $VO(acac)_2$ into the solution catalyzes the decomposition of H_2O_2, and the substrate is completely consumed in 30 min after mixing the reagents.[1] The conversion of *n*-alkanes increases in proportion with the initial hydrogen peroxide concentration $[H_2O_2]_0$; for example, the 50% conversion of *n*-octane is achieved at a 12-fold molar excess of the oxidant. It should be noted that conventional inhibitors of free radical chain reactions—BHT, *p*-benzoquinone, or anthracene derivatives (10 mol % of the substrate concentration)—have no effect on both the substrate consumption rate and composition of oxidation products. The oxidation rate of inhibitors, for example, of BHT, does not exceed the substrate consumption rate. *p*-Benzoquinone is not oxidized at all under these conditions. These observations point to a nonchain oxidation mechanism in the V^V/H_2O_2/AcOH system.

The products of *n*-alkane oxidation contained both secondary alcohols and ketones with the same carbon backbone as in the initial alkane (table); neither the oxidative destruction nor isomerization of a carbon chain was observed. This is consistent with the nonchain character of the process. The terminal methyl groups of an *n*-alkane are not involved in the reaction, and only secondary carbon atoms are oxidized. For example, the oxidation of *n*-heptane gave rise to 2-heptanol, 3-heptanol, 4-heptanol, 2-heptanone, 3-heptanone, and 4-heptanone. Neither hexanol-1 nor heptanal was found among the reaction products.

The overall yield of alcohols and ketones was ~60% at a substrate conversion of ~35%. The content of ketones in the products of *n*-alkane oxidation was considerably higher than that of the corresponding alcohols (table, figure). No hydroxy ketones were formed upon the oxidation of *n*-heptane or lower alkanes.

Alcohols and ketones are the ultimate products of alkane oxidation in the system under consideration; alcohols are not intermediates in the formation of ketones. For example, in the course of concurrent oxidation of 0.01 M of 3-pentanol and 0.1 M of *n*-octane ($[H_2O_2]_0$ = 1 M), the alcohol was not consumed. Upon the concurrent oxidation of 2-butanol (0.01 M) and *n*-octane (0.1 M), the final 2-butanol concentration did not exceed 0.001 M after all the H_2O_2 ($[H_2O_2]_0$ = 1 M) was consumed. The products accumulate without the induction period, and the curve of alcohol accumulation has no maximum (figure). These observations suggest that alcohols and ketones are formed from corresponding alkanes in parallel reactions. The oxidation of linear alkanes resembles the oxidation of cyclohexane [8].

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[1] Using ammonium vanadate instead of vanadyl acetylacetonate has no effect on the composition of reaction products, as well as on the conversion of a substrate. The EPR spectra of reaction solutions showed that, in the presence of either of these compounds as a catalyst, the signals that arose from V^{IV} were not observed until hydrogen peroxide was completely exhausted. This permits the conclusion that the oxidative system is largely composed of V^V complexes, which catalyze the reactions observed.

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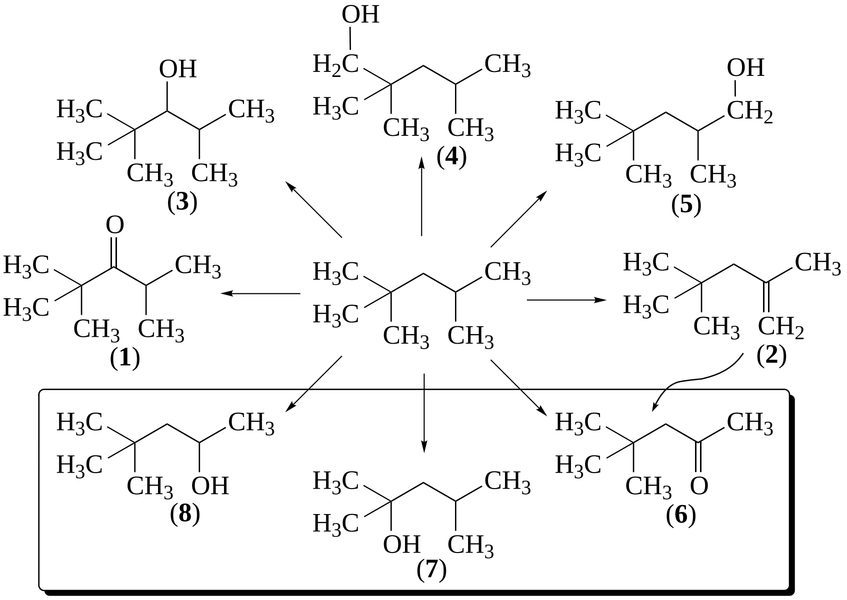
Indeed, as in the case of *n*-alkanes, the oxidation of cyclohexane in the V^V/H_2O_2/AcOH system results in cyclohexanol and cyclohexanone (formed in parallel reactions), and no >C–C< bond cleavage is observed [8]. The only difference is that the ratio [ketone]/[aldehyde] ~ 1 is typical of the oxidation of cyclohexane, whereas this ratio for alkanes slightly depends on the position of a ruptured CH bond in a carbon chain but is always more than unity. The suggested mechanism of cyclohexane oxidation implies the formation of an active oxidant in the rate-limiting stage; this active oxidant can both oxidize the substrate and undergo deactivation to produce O_2. In this case, the reactivity of the substrate varies in inverse proportion to the H_2O_2 excess, all other things being the same. Given that this mechanism is also valid for the oxidation of linear alkanes, relative reactivities of substrates can be estimated based on the relative rate constants of *n*-alkane oxidation calculated from the data on competitive oxidation of alkanes and cyclohexane [11].

The reactivities of linear alkanes, other than *n*-pentane, are slightly lower than the reactivity of cyclohexane; the corresponding relative oxidation rate constants range from 0.5 to 1.5. In other oxidative systems, cyclohexane is also more active than *n*-alkanes [1–3].

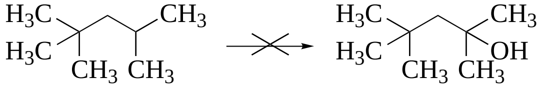
Unexpected results were obtained for the oxidation of isooctane in the V^V/H_2O_2/AcOH system. The isooctane molecule has only one methylene group; thus, by analogy with the oxidation of cyclohexane and *n*-alkanes, the oxidation of isooctane should result only in 2,2,4-trimethyl-3-pentanone (**1**) and 2,2,4-trimethyl-3-pentanol (**3**) (Scheme 1). However, GC-MS evidence showed the formation of the following oxidation products: 2,2,4-trimethyl-3-pentanone (**1**) as a major product, 2,4,4-trimethyl-1-pentene (**2**), 2,2,4-trimethyl-3-pentanol (**3**), 2,2,4-trimethyl-1-pentanol (**4**), 2,4,4-trimethyl-1-pentanol (**5**), 4,4-dimethyl-2-pentanone (**6**), 2,4-dimethyl-2-pentanol (**7**), and 4,4-dimethyl-2-pentanol (**8**) (Scheme 1). In contrast to *n*-alkanes, isooctane is oxidized to form, among other products, primary alcohols.



Scheme 1. Identified products of isooctane oxidation in the V^V/H_2O_2/AcOH system.

The formation of 2,4,4-trimethyl-1-pentene (**2**) points to the oxidative dehydrogenation of isooctane. Similar reactions were observed for the oxidation of cyclooctane by the GIF system (Fe^{III} salts/ *tert*-butyl-hydroperoxide) [12]. In this context, the formation of 4,4-dimethyl-2-pentanone (**6**) (Scheme 1) could be explained by the oxidative dehydrogenation of isooctane and by the oxidative splitting of 2,4,4-trimethyl-1-pentene (**2**) forming in the V^V/H_2O_2/AcOH system [9, 10]. However, the formation of 2,4-dimethyl-2-pentanone (**7**) and 4,4-dimethyl-2-pentanone (**8**) strongly suggests the C–C bond cleavage.

The surprising thing is that the reaction mixture lacked the products of hydroxylation of isooctane at the tertiary carbon atom, such as, for example, 2,4,4-trimethyl-2-pentanol.



(1)

This alcohol or its acetate may presumably undergo dehydration or AcOH elimination to produce 2,4,4-trimethyl-1-pentene (**2**) found among the reaction products.

The most surprising thing in the oxidation of isooctane in the V^V/H_2O_2/AcOH system is the oxidative C–C bond rupture. First, oxidizable impurities that may attend the initial isooctane were suspected to be responsible for the occurrence of C_7 hydrocarbons (such as

Oxidation of *n*-alkanes in the V^V/H_2O_2/AcOH system at 30°C, $[V^V] = 4 \times 10^{-3}$ M, and $[H_2O_2]_0 = 1$ M

No.	*n*-Alkane	Concentration, M	Conversion, %	$[\text{alcohol}]_{\text{total}} \times 10^4$, M	$[\text{ketone}]_{\text{total}} \times 10^3$, M
1	Pentane	0.1	49	45[a]	40[b]
2	Hexane	0.1	32	37[c]	25[d]
3	Heptane	0.1	32	24[e]	18[f]
4	Octane	0.1	30	32[g]	20[h]
5	Nonane	0.05	31	18	9[i]
6	Decane	0.05	29	22	8
7	Tetradecane	0.05	21	33	6
8	Pentadecane	0.05	16	23	5
9	Hexadecane	0.05	15	18	5
10	Nonadecane	0.05	11	21	3
11	Pentane BHT	0.1 0.01	47	43	38

Note: [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.

4,4-dimethyl-2-pentanone (**6**), 2,4-dimethyl-2-pentanol (**7**), and 4,4-dimethyl-2-pentanol (**8**)) among the reaction products. However, the purity of the starting isooctane was higher than 99.8%, and the content of 2,2-dimethylpentane and 2,4-dimethylpentane was no more than 0.02%.[2] These minute amounts of C_7 alkanes are insufficient to explain the formation of noticeable amounts (no less than 2% of the stating isooctane) of **6**, **7**, and **8**. Correspondingly, the formation of 4,4-dimethyl-2-pentanone (**6**), 2,4-dimethyl-2-pentanol (**7**), and 4,4-dimethyl-2-pentanol (**8**) cannot be attributed to the admixtures of isomeric hexanes in the starting substrate. Therefore, all available data indicate that the C_7 alcohols and ketones originate from isooctane, and its oxidation involves the oxidative destruction of a C–C bond.

Another evidence in favor of the C–C bond cleavage in reactions catalyzed by the V^V/H_2O_2/AcOH system was provided by the oxidation of fatty acids methyl esters (FAMEs).

As in *n*-alkane oxidation, the FAME conversion monotonically increases with an increase in the initial H_2O_2 concentration ($[H_2O_2]_0$). The limiting substrate conversion (η_∞)—the conversion achieved after all H_2O_2 was exhausted—constitutes 90% at a tenfold molar excess of H_2O_2. Our findings indicate that the relative FAME reactivity increases with an increase in the number of carbon atoms in the FAME chain: the higher the molecular weight of the ester, the lower the H_2O_2 excess required to achieve the desired η_∞ value. The oxidation of FAMEs results in alcohols and ketones functionalized at different sites of the aliphatic chain of an initial ester. For example, the oxidation of methyl octanoate yields three octanoic acid isomers identified in the form of trimethylsilyl esters.[3] In addition to the products with the same length of the hydrocarbon chain as in the starting FAME, the oxidation products of methyl octanoate contain at least three isomers of hydroxyheptanoic acid, three isomers of hydroxyhexanoic acid, three isomers of hydroxypentanoic acid, and two isomers of hydroxybutanoic acid. Hydroxy acids and keto acids were found among the oxidation products of other FAMEs.

A good solubility of the reaction products in water and their tendency toward polycondensation make the quantitative analysis of a reaction mixture difficult. However, the chromatograms of the oxidation products of all FAMEs show a peak corresponding to a glycolic acid ester. In some experiments, the ester is a major product, as judged from the chromatographic peak intensity.

Glycolic acid originates from an FAME rather from the solvent (AcOH). Thus, the oxidation of methyl isobutanoate does not result in the formation of glycolic acid. In addition, the GC-MS analysis of the silylated products of the oxidation of methyl stearate in CD_3COOD showed that the reaction mixture contains only the nondeuterated trimethylsilyl glycolate $(CH_3)_3SiOCH_2COOSi(CH_3)_3$. The lack of deuterium atoms in the OCH_2COO moiety of glycolic acid excludes the formation of it from the solvent.

The oxidation of FAMEs in the V^V/H_2O_2/AcOH system involves oxidative destruction, as demonstrated by the formation of glycolic acid and its esters and other products with a shortened hydrocarbon chain compared to a starting FAME.

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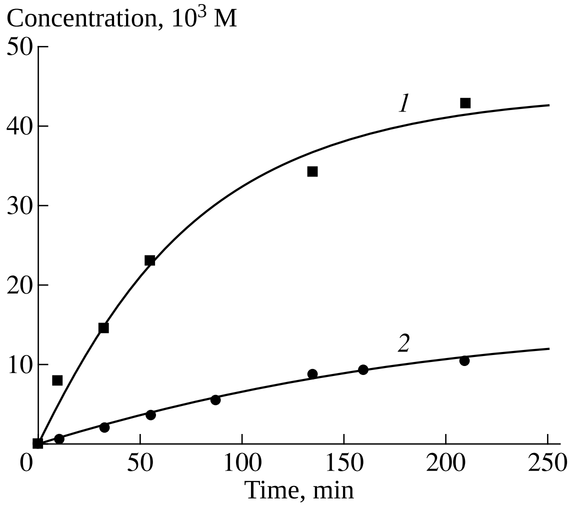
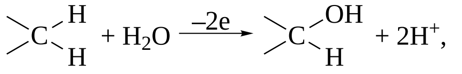
[2] As determined by GC-MS (a 100-m SPB-1 capillary column 0.25 mm in i.d.).

[3] The reaction mixture of the FAME oxidation was silylated with bis(trimethylsilyl)trifluoroacetamide at room temperature, and the resulting trimethysilyl esters were extracted with chloroform and analyzed by GC-MS.

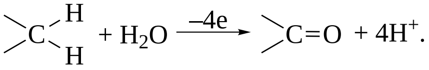


Accumulation of (*1*) pentanone and (*2*) pentanol in the course of oxidation of *n*-pentane in the $V^V/H_2O_2/AcOH$ system at 30°C, $[V^V] = 4 \times 10^{-3}$ M, $[S]_0 = 0.1$ M, and $[H_2O_2]_0 = 1$ M.

The oxidative splitting of C–H bonds at a tertiary or quaternary carbon atom to produce either ketones or secondary or tertiary alcohols, as well as analogous reactions in the case of cyclohexane, can be schematically represented as two- or four-electron removal:

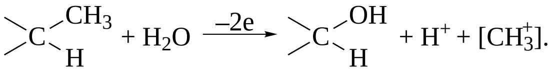


$$>C\begin{smallmatrix}H\\H\end{smallmatrix} + H_2O \xrightarrow{-2e} >C\begin{smallmatrix}OH\\H\end{smallmatrix} + 2H^+, \tag{2}$$



$$>C\begin{smallmatrix}H\\H\end{smallmatrix} + H_2O \xrightarrow{-4e} >C{=}O + 4H^+. \tag{3}$$

A similar scheme can be suggested for C–C bond splitting:



$$>C\begin{smallmatrix}CH_3\\H\end{smallmatrix} + H_2O \xrightarrow{-2e} >C\begin{smallmatrix}OH\\H\end{smallmatrix} + H^+ + [CH_3^+]. \tag{4}$$

$[CH_3^+]$ in reaction (4) symbolizes a cationic species trapped by a solvent molecule in the transition state, which further transforms to methyl acetate.

The methyl CH bonds in isooctane can be oxidized to produce primary alcohols; however, their yield is small. Five CH_3 groups of the isooctane molecule contain 15 CH bonds per two methylene bonds and one CH bond at the tertiary C atom. Therefore, the low yield of primary alcohols indicates that the activity of methyl groups in this reaction is lower than the activities of CH_2- and CH groups.

The electronegative CH_3OOC groups in FAME molecules might be expected to suppress the reactivity of the aliphatic chain in oxidation. However, the FAME oxidation rates do not significantly differ from the oxidation rates of cyclohexane and alkanes. Similar to alkanes, the FAME molecule is oxidized to produce the corresponding hydroxy and keto acids and their esters. The propensity of the carboxy group of the FAME molecule to coordinate vanadium(V) can influence both the rate and selectivity of oxidation. This argument should be taken into account to rationalize the surprising easiness of C–C bond cleavage in the course of FAME oxidation.

Our findings indicate that the oxidation of FAMEs in the $V^V/H_2O_2/AcOH$ system does not involve free radical chain reactions. However, it is conceivable that the C–C bond cleavage involves electron transfer from hydrocarbon C atoms to the vanadium(V) complex. Similar transformations were observed in the course of Co^{II}/Co^{III}-catalyzed alkane oxidation by dioxygen in a CF_3COOH solution [13, 14].

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