Oxidation with the "O_2—H_2O_2—vanadium complex—pyrazine-2-carboxylic acid" reagent
9.* Oxidation of cyclohexene and decalin

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The oxidation of cyclohexene with hydrogen peroxide catalyzed by a vanadium complex and pyrazine-2-carboxylic acid (PCA) in air results in the formation of cyclohex-2-enyl hydroperoxide as the main product and cyclohex-2-enol, cyclohex-2-enone, cyclohex-3-enyl hydroperoxide, cyclohex-3-enol, cyclohexanol, cyclohexane, and 1,2-epoxycyclohexane in lesser amounts. The composition of the products of oxidation of decalin isomers with the system in question is similar to those obtained in the photochemical oxidation with hydrogen peroxide in air and in the oxidation with air in the presence of anthraquinone. A proposed mechanism for the oxidation includes the initiation by hydroxyl radicals generated from hydrogen peroxide under the action of the V—PCA system.

Key words: activation of C—H bond, alkanes, hydroxyl radicals, decalin, metallocomplex catalysis, oxidation, hydrogen peroxide, vanadium complexes, cyclohexene.

Activation of chemical bonds in hydrocarbons by metal complexes is an important area of modern chemistry.[2,3] One of the pathways of conversion of these compounds into valuable products is their oxidation by molecular oxygen, peroxides, and other donors of oxygen atoms. Thus, saturated hydrocarbons can be catalytically converted into alkyl peroxides, ketones, alcohols, and carboxylic acids, while aromatic compounds are mainly converted into phenols and quinones, whereas oxidation of olefins results in the formation of epoxides and ketones. Oxidation of the least reactive hydrocarbons, *viz.*, alkanes, in the presence of a metallocomplex catalyst often proceeds under relatively mild conditions and is more selective than non-catalytic processes. The reactivity of unsaturated hydrocarbons is substantially higher; however, the use of a metallocomplex catalyst makes it possible to increase both the product yield and selectivity even for these compounds. Usually, olefins enter into various reactions involving the two most reactive fragments of their molecules, namely, the double bonds themselves and the C—H bonds in α-position to the double bond.

Previously,[4—13] we have shown that hydrogen peroxide effectively oxidizes various organic compounds in acetonitrile in the presence of catalytic amounts of vanadate anion and pyrazine-2-carboxylic acid (PCA) in air. Some other vanadium derivatives are also active as catalysts. In the absence of PCA, the rate of oxidation is low. Picolinic acid and some other chelating ligands accelerate oxidation, but to a lesser extent than PCA. It has been established that saturated hydrocarbons are converted into alkyl hydroperoxides, ketones (aldehydes), and alcohols, arenes are mostly converted into phenols and quinones, whereas alcohols are converted into ketones (aldehydes). Methane[1,13] and ethane[1,8,13] are converted into formic and acetic acid, respectively. No oxygenation of alkanes occurs if at least one of the components of the catalytic system or air is absent. The oxidation of cyclohexane in an atmosphere of $^{18}O_2$ showed[1,13] that the oxygenation products contain considerable amount of ^{18}O; thus, it can be concluded that hydrogen peroxide acts as promoter in the oxidation of alkanes, whereas molecular oxygen is the true oxidant.

At room temperature, alkanes are mostly converted into alkyl hydroperoxides and to a lesser extent into alcohols and ketones. It is noteworthy that in the oxidation of cyclohexane at low temperature cyclohexanone and cyclohexanol are formed in the initial stage of the process simultaneously with cyclohexyl hydroperoxide.[9] At elevated temperatures (50—70 °C), the peroxide decomposes relatively quickly yielding a ketone and an alcohol. Based on the previously obtained results, a

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* For Part 8, see Ref. 1.

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conclusion was drawn that the "H_2O_2—VO_3^-—PCA" reagent is an efficient generator of hydroxyl radicals, which attack the substrate molecule.[4—13] The "VO_3^-—PCA" pair catalyzes the reaction with an appreciably higher efficiency as compared to the Fenton reagent, which usually contains equivalent amounts of Fe^{II} and H_2O_2.

In this work, we study the oxidation of hydrocarbons with relatively weak C—H bonds (tertiary bonds in decalin isomers and allylic bonds in cyclohexene) with the "O_2—H_2O_2—VO_3^-—PCA" reagent.

Experimental

The oxidation of hydrocarbons was carried out in air in cylindrical glass vessels with intense stirring at constant temperature. The volume of the reaction solution was 10 mL. A portion of 30% aqueous H_2O_2 ("Merck", São Paulo) was added to a solution of the catalyst (in all cases, $0.1 \cdot 10^{-3}$ mol L^{-1} $Bu^n{}_4NVO_3$ [14] and $0.4 \cdot 10^{-3}$ mol L^{-1} PCA) and hydrocarbon (0.47 mol L^{-1}) in MeCN.

The reaction mixture was analyzed by GLC before and after addition of an excess of triphenylphosphine using a Hewlett—Packard Series II. 5890 chromatograph equipped with a quartz-reinforced injector, a flame ionization detector, a quartz Carbowax 20M column (25 m × 0.2 mm; 0.2 μm), and a Shimadzu CR3A integrator. Helium was used as the carrier gas. The peaks were identified by chromato-mass spectrometry on a Shimadzu GC-17A-QP 5000 GLC-MS instrument (Innowax, 25 m × 0.2 mm; 0.4 μm) using the data of The Wiley 139 Database Library. The quantitative analysis was performed after calibration of the chromatograms using authentic compounds.

Acetonitrile (HPLC grade, 99.99%, EM Science, Darmstadt) and cyclohexene (Aldrich) were distilled prior to use in the reaction. Decalin isomers (Aldrich) were used without additional purification.

Results and Discussion

The compositions of the products obtained in the oxidation of *cis*- and *trans*-decalin with the reagent under study, in the photoinduced oxidation of the same compounds in acetonitrile with the O_2—H_2O_2 system in air (as is well known,[15] the latter reaction proceeds with the formation of hydroxyl radicals), and in the oxidation with O_2 in water[16] in the presence of anthraquinone as sensitizer are listed in Table 1. Both latter reactions proceed according to the following scheme:

$$RH + M^{\cdot} \longrightarrow R^{\cdot} + M{-}OH,$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}.$$

Here RH is a hydrocarbon and $M^{\cdot}$ is the hydroxyl radical $HO^{\cdot}$ or photoexcited anthraquinone. The $ROO^{\cdot}$ radical is then converted into a mixture of ROOH, ROH, and $R'_2C{=}O$. Under the action of triphenyl-

Table 1. Composition of the oxidation products of *cis*- and *trans*-decalin in various systems

Product	Composition (%)			
	O_2—H_2O_2—VO_3^-—PCA[a]	O_2—H_2O_2—$h\nu$[a]	O_2—anthraquinone[b]	$VO(O_2)(Pic) \cdot 2H_2O$[c]
		cis-Decalin		
trans-Decalin-9-ol (**A**)	28.4	29.0	46.8	1.0
cis-Decalin-9-ol (**B**)	6.0	6.5	10.0	6.9
cis-Decalin-1-ol	13.0	20.5	4.0	2.4
cis-Decalin-2-ol	32.0	34.0	7.5	0.4
cis-1-Decalone	11.0	5.0	1.9	3.7
cis-2-Decalone	10.0	5.0	12.6	2.2
trans-1-Decalone	—	—	16.9	—
A/**B** ratio	4.7	4.5	4.7	0.14
		trans-Decalin		
trans-Decalin-9-ol (**A**)	17.0	19.0	18.2	
cis-Decalin-9-ol (**B**)	3.5	4.0	3.8	
trans-Decalin-1-ol	21.5	31.0	12.4	
trans-Decalin-2-ol	33.0	35.5	30.0	
trans-1-Decalone	14.0	5.5	19.9	
trans-2-Decalone	11.0	5.0	14.6	
cis-1-Decalone	—	—	1.0	
A/**B** ratio	4.9	4.8	4.8	
γ[d] ratio	1.7	1.5	2.6	

[a] The reaction mixture was treated with triphenylphosphine before GLC analysis; see also Ref. 9.

[b] Some other products at low concentrations were also detected; data taken from Ref. 16.

[c] Pic is the picolinate-anion. The yields (%) are reported with respect to the vanadium complex; data taken from Ref. 17.

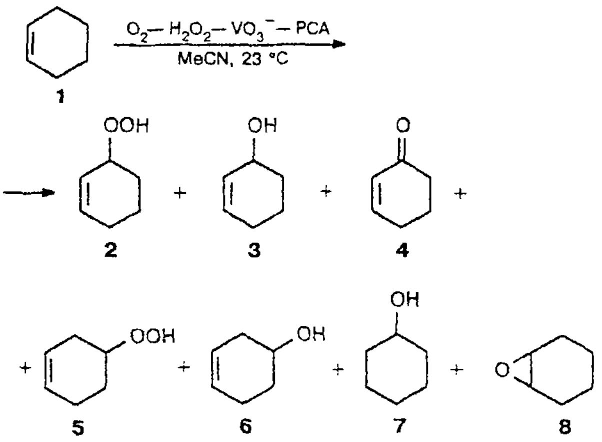
[d] γ = [(*trans*-decalin-9-ol + *cis*-decalin-9-ol) from *cis*-decalin] / [(*trans*-decalin-9-ol + *cis*-decalin-9-ol) from *trans*-decalin].

phosphine, hydroperoxide ROOH is readily converted into ROH. It follows from the data in Table 1 that the ratios of *trans*- and *cis*-decalin-9-ols formed (**A**/**B**) are very close for all three reactions. This confirms the assumption that hydroxyl radicals play a key role in the oxidation with the "O_2—H_2O_2—VO_3^-—PCA" reagent. The ratios of the total amounts of these decalinols obtained from *cis*- and *trans*-decalins $(\mathbf{A} + \mathbf{B})_{cis}/(\mathbf{A} + \mathbf{B})_{trans}$ (see Table 1, parameter γ) for the oxidation with the "O_2—H_2O_2—VO_3^-—PCA" and "O_2—H_2O_2—$h\nu$" systems (1.7 and 1.5, respectively) are much lower than in the case of the oxidation sensitized by anthraquinone (2.6). This difference can be due to a lesser steric shielding in the case of attack of the C —H bond by the hydroxyl radical. Actually, the tertiary C—H bonds strongly shielded in *trans*-decalin are relatively less accessible for steric reasons if a bulky reagent (namely, the molecule of photoexcited anthraquinone) abstracting the H atom is used. It is remarkable that in the oxidation of *cis*-decalin with the Mimoun complex $VO(O_2)(Pic) \cdot 2H_2O$ (Pic is the anion of picolinic acid) in acetonitrile at 20 °C the **A**/**B** ratio is only 0.14.[17] The formation of *trans*-decalin-9-ol indicates that the 9-decalyl radical is also produced in this process, and its inversion occurs to a certain extent. In spite of this, the low value of the above parameter points to the fact that the nature of the radical-like species generated from the Mimoun complex differs from that of the active species in the "O_2—H_2O_2—VO_3^-—PCA" system. The distinction between these systems is also reflected in the yields of the products normalized with respect to the number of secondary and tertiary C—H bonds in decalin. Thus, the 2° : 3° ratio for the reaction under study is approximately equal to 1 : 4, whereas for the reaction with peroxo complex this ratio is equal to 1 : 17. It can be assumed that in the former complex the H atom is abstracted from the decalin molecule by a bulkier species, for instance, by the V^{IV}—OO$^\cdot$ complex, whereas the latter system is a generator of hydroxyl radicals.

It was of interest to use the reagent under study for oxidizing other hydrocarbons with weak C—H bonds, for instance, olefins containing the allylic H atoms in the molecule, cyclohexene (**1**), in particular.

The oxidation of **1** taken in excess relative to H_2O_2 and the $Bu^n{}_4NVO_3$+PCA (1 : 4) catalytic pair was carried out under analogous conditions. As was shown previously,[4—13] this ratio provides the highest rate of cyclohexane oxidation. It should be noted that in the oxidation of cyclohexane with Gif systems picolinic acid was used[18] as a cocatalyst strongly accelerating the reaction in an iron complex : picolinic acid (1 : 4) system. The process was monitored by withdrawing aliquots of the reaction solution at specific intervals and analyzing them by GLC. Each sample was analyzed before and after addition of an excess of triphenylphosphine, which made it possible to calculate real concentrations of peroxides, alcohols, ketones, and other compounds present in the solution at the moment[1,4—13,19—21] (see also, for instance, Refs. 22 and

Scheme 1



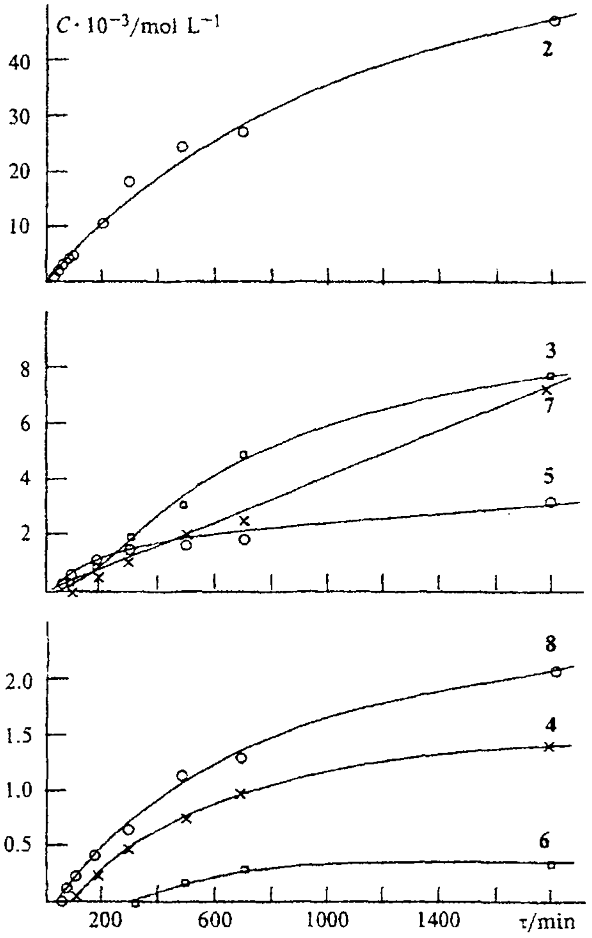


Fig. 1. The kinetics of cyclohexene oxidation with the "O_2—H_2O_2—VO_3^-—PCA" reagent at 23 °C (**2**—**8** are the compounds shown in Scheme 1).

23). The products formed in the oxidation of **1** and identified by chromato-mass spectrometry are shown in Scheme 1.

The accumulation of all seven products (**2**—**8**) as a function of time is shown in Fig. 1. The cleavage of the weakest allylic C—H bond results in cyclohex-2-enyl hydroperoxide (**2**), which is the main reaction product. Cyclohex-2-enol (**3**) and especially cyclohex-2-enone (**4**) and cyclohex-3-enyl hydroperoxide (**5**) are formed in appreciably smaller amounts. Thus, the ratio of concentrations of hydroperoxides **2** and **5** and that of alcohols **3** and **6** after 1800 min is equal to 22 and 30, respectively. The amount of the cyclohexene derivative with the carbonyl group in the β-position is small.

It is remarkable that cyclohexanol **7** is also among the oxidation products; its concentration amounts to $7.5 \cdot 10^{-3}$ mol L^{-1} after 1800 min. In contrast to other products, for which the rate of accumulation decreases more or less sharply after 700 min, the concentration of **7** increases linearly over the whole reaction period. 1,2-Epoxycyclohexane **8** is also formed in this reaction, but in a much smaller amount as compared to hydroperoxide **2**, the (**2**) : (**8**) ratio is equal to 24 after 1800 min. The overall concentration of all the products after this period of time amounts to $67.3 \cdot 10^{-3}$ mol L^{-1}. Thus, the yield of the products with respect to H_2O_2 and the turnover number of the catalyst, which was equal to 675, is 34%. In this calculation we assumed that one molecule of hydrogen peroxide is required for the formation of one molecule of the product.

It can be seen in Fig. 1 that the accumulation of hydroperoxide **2** occurs at a maximum rate in the initial stage of the reaction, whereas for all other products it begins only after the induction period. It can be assumed that alcohol **3** and ketone **4** are formed upon decomposition of hydroperoxide **2**, while hydroperoxide **5** is a precursor of alcohol **6**. Previously,[9] we have noted that in the oxidation of the more inert saturated hydrocarbon, cyclohexane, with the same reagent at 50—70 °C not only cyclohexyl hydroperoxide, but also cyclohexanol and cyclohexanone, were formed simultaneously in the initial stage of reaction.

Hydroperoxides **2** and **5** can be formed as follows. Under the action of the vanadium-containing catalyst, hydroxyl radicals are efficiently generated from H_2O_2. The reduction of V^V and subsequent reaction of V^{IV} with H_2O_2 are most likely the key stages of this process:

$$V^V{=}O + H_2O_2 \longrightarrow V^{IV}{-}OH + HOO^{\cdot},$$

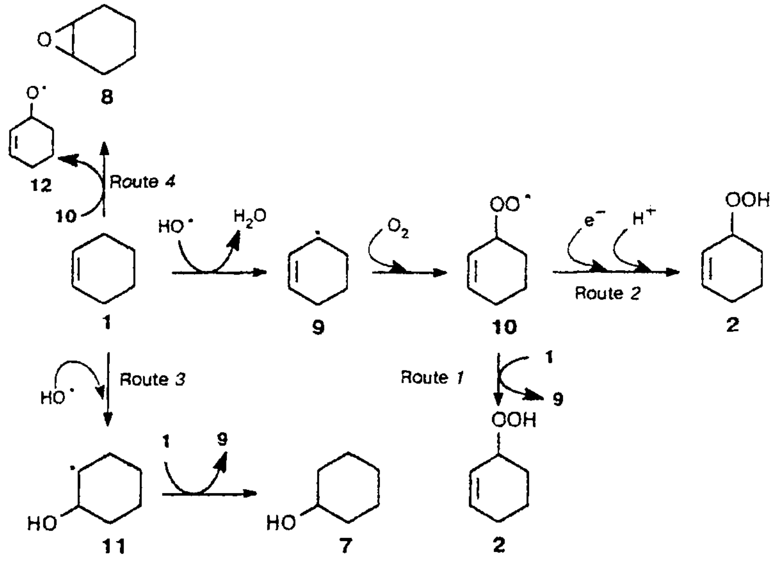
$$V^{IV}{-}OH + H_2O_2 \longrightarrow V^V{=}O + H_2O + HO^{\cdot}.$$

The hydroxyl radical attacks cyclohexene **1** mainly on the weakest allylic C—H bond yielding radical **9** (Scheme 2), which adds an oxygen molecule and is rapidly converted into radical **10**. The alkylperoxyl radicals produced from saturated hydrocarbons are most likely incapable of abstracting the hydrogen atom from the alkane molecule at ambient temperature. On the contrary, in the presence of **1** having weak allylic C—H bonds such radicals including **10** are capable of cleaving these bonds (R is cyclohex-2-enyl):

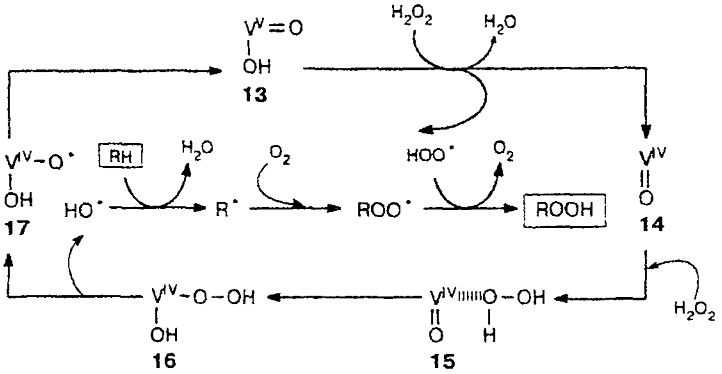
$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}.$$

At 10 °C, the rate constant and activation energy (E_a) of the reaction are equal to 0.6 L mol^{-1} s^{-1} and 35.6 kJ mol^{-1}, respectively.[24] The reaction results in the formation of peroxide **2** and the new radical **9** and imparts the chain character to the process (see Scheme

Scheme 2



Scheme 3



2, route *1*). However, since H_2O_2 acts as a stoichiometric promoter rather than the reaction initiator, the chain process is most likely not the main route from cyclohexene **1** to peroxide **2**. Actually, the peroxo radical **10** can be reduced, for instance, with a V^{IV} compound to yield hydroperoxide **2** after addition of a proton (route *2*). Radical **10** can also be converted into **2** in the reaction with the HOO· radical produced in the first stage of the process:

$$ROO^{\cdot} + HOO^{\cdot} \longrightarrow ROOH + O_2.$$

In the alternative route *3* (see Scheme 2), the hydroxyl radical is added to the double bond of cyclohexene **1** and the adduct obtained, radical **11**, then abstracts the H atom from **1**, producing **7**. The contribution of termination according to Russel[25] in the disproportionation of ROO· radicals

$$ROO^{\cdot} + ROO^{\cdot} \longrightarrow ROOOOR \longrightarrow ROH + R'_2C{=}O + O_2,$$

is most likely small, since in this case an alcohol and a ketone had to be generated simultaneously with ROOH. The mechanism of the formation of epoxide **8** is less clear. The plausible route *4* (see Scheme 2) includes the reaction of **1** with radical **10**. The latter is converted into radical **12**, which yields alcohol **3** after abstraction of the H atom from the second molecule of **1**. The epoxide can also be obtained following a parallel non-radical route in the catalysis with a vanadium derivative (for epoxidation of olefins using peroxovanadium complexes see, for example, Refs. 26—29). Hydrogen peroxide and/or hydroperoxide **2** can play the role of epoxidizing reagent in such a process.

A plausible catalytic cycle for vanadium-catalyzed conversion of a hydrocarbon RH into the corresponding hydroperoxide ROOH is shown in Scheme 3. The chain radical process, which is possible when using **1**, is not shown in this simplified scheme. The reaction between the starting compound V^V conventionally denoted as $V^V(OH){=}O$ (**13**) and the first H_2O_2 molecule gives oxocomplex V^{IV} (**14**) and the HOO· radical. After addition of the second H_2O_2 molecule, the peroxo complex **16** is formed, which decomposes generating a hydroxyl radical and a species **17**. The latter can be considered as a resonance form of the starting compound **13**. According to this reaction scheme, two H_2O_2 molecules and one molecule of molecular oxygen are required to form ROOH from RH. The assumption made is in agreement with the observation[4—13] according to which the maximum yield of the oxygenation products with the reagent under discussion did not exceed 1 mole per 2 moles of H_2O_2 and in some cases was close to this value. The hydroperoxide in Scheme 3 is formed in the reaction between ROO· and HOO· radicals, which makes it possible to formally close the complete catalytic cycle. Naturally, some other routes are also possible (for instance, the chain radical process mentioned above). The accelerating role of PCA is unclear. However, it can be assumed that this ligand is a reservoir of electrons (analogously to that assumed in the case of porphyrinate and polyoxometalate catalysis[30,31]) and facilitates one of the stages of the catalytic cycle, for instance, the reduction of **13** to **14**.

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