

Oxidations by a $\text{H}_2\text{O}_2\text{—VO}_3^-$ —pyrazine—2-carboxylic acid reagent

1. Oxidation of alkanes in CH_3CN to produce alkyl peroxides*

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Alkanes (cyclohexane, hexane, heptane isomers) are effectively oxidized in CH_3CN at 20–70°C by hydrogen peroxide when catalyzed by a $\text{Bu}_4\text{NVO}_3^-$ —pyrazine—2-carboxylic acid system. Alkyl hydroperoxide is the main product; an alcohol and a ketone or an aldehyde are also formed. Under these conditions benzene is oxidized to give phenol, while alkyl benzenes yield oxygenation products both of the ring and the side chain. It has been assumed that the interaction of H_2O_2 with VO_3^- gives rise to generation of HO^\cdot radicals and other radical-like vanadium containing species that abstract a hydrogen atom from an alkane, RH . The radical R^\cdot formed reacts with O_2 to produce ROO^\cdot which is then transformed to alkyl hydroperoxide.

Key words: alkanes, oxidation, homogeneous catalysis, hydrogen peroxide, vanadium, hydroxyl radicals.

Hydrogen peroxide is extensively used to oxidize organic substances; many reactions of this kind proceed with the participation of compounds of the transition metals.^{1–6} The merits of this oxidizing agent are its availability, low cost, and the fact that oxygen and water are the only by-products in the reactions. The oxidation reactions of saturated and aromatic hydrocarbons by hydrogen peroxide catalyzed by metal complexes are of particular interest.^{4,5} For instance, articles have recently been published describing the oxidation of the C–H bond in hydrocarbons catalyzed by oxocomplexes of chromium,^{7,8} polyoxometallates,^{9,10} metalloporphyrins,^{11–13} compounds of titanium,¹⁴ ruthenium,^{15,16} iron,^{17–24} palladium,²⁵ and vanadium.^{26–29} However, not all of these methods are suitable for synthesizing products of hydro-

carbon oxygenation. Thus, the oxidation by Gif systems proceeds in pyridine only,^{18,19} the oxidation of alkanes catalyzed by porphyrin complexes of manganese requires a high imidazole concentration,¹¹ while the oxygenation of cyclohexane and other hydrocarbons in acetic and trifluoroacetic acid catalyzed by oxocomplexes of vanadium requires high H_2O_2 concentrations, and the efficiency of the peroxide use is not high.²⁸ It is also to be noted that the well known Fenton's reagent is not an efficient oxidizer for hydrocarbons.

The peroxide complexes of vanadium(V) hydroxylate hydrocarbons^{26,30} and other organic substances³¹ in a stoichiometric reaction, whereas a series of vanadium compounds are catalysts of oxidation by hydrogen peroxide.^{26–29,32}

In continuing the study of processes of oxidizing alkanes by hydrogen peroxide catalyzed by transition metal complexes (the catalysis by oxocomplexes of chro-

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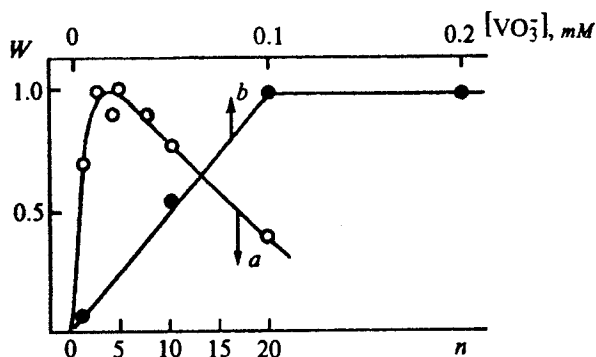


Fig. 1. Dependences of relative initial rates of cyclohexane oxidation W (found from accumulation of products) on the ratio n , $[\text{PCA}]:[\text{VO}_3^-]$ (a) and on $[\text{VO}_3^-]$ (b). Reaction conditions: 60°C , $0.2\text{ M H}_2\text{O}_2$. a, $[\text{VO}_3^-] = 10^{-4}\text{ M}$; b, $[\text{PCA}] = 4[\text{VO}_3^-]$. $[\text{C}_6\text{H}_{12}] = 0.232\text{ M}$.

mium has been presented in ref.^{7,8}), we attempted to use vanadium(V) compounds as catalysts. It has been found that cyclohexane is not oxidized by H_2O_2 in acetonitrile if the vanadate ion is used in the form of the tetrabutylammonium salt, Bu_4NVO_3 , as the catalyst. However, on addition of an organic compound, which can serve as a chelating agent, into the reaction medium, a more or less rapid accumulation of the alkane oxygenation products can be detected. Salicylic and anthranilic acid, L-alanine, and 8-hydroxyquinoline are used as cocatalysts. The oxidation proceeds more vigorously if 2-picolinic and especially pyrazine-2-carboxylic acids are employed. In the present work, the latter has been chosen as a cocatalyst in order to carry out the oxygenation of a series of saturated and aromatic hydrocarbons by hydrogen peroxide.

Experimental

The experiments on oxidation were carried out at constant temperature in cylindrical vessels equipped with reflux condensers, in air with intensive stirring. The total volume of the reaction solution was 10 ml. Initially, a 30% aqueous solution of hydrogen peroxide (Aldrich) was added to the solution. The process was monitored by withdrawing aliquots at specific intervals and analyzing them by means of GLC (each sample was analyzed twice, i.e. before and after the addition of triphenylphosphine). For the analysis, a Perkin-Elmer 8500 chromatograph (the columns 2 m in length with 5% Carbowax on Chromosorb W 80/100, the carrier gas was helium) and an HP 3390A integrator were employed. Before each experiment, acetonitrile used as the solvent was distilled from CaH_2 under nitrogen.

Results and Discussion

We have found that hydrogen peroxide effectively oxidizes cyclohexane in acetonitrile at $20\text{--}70^\circ\text{C}$, provided that the vanadate ion as its tetrabutylammonium salt,

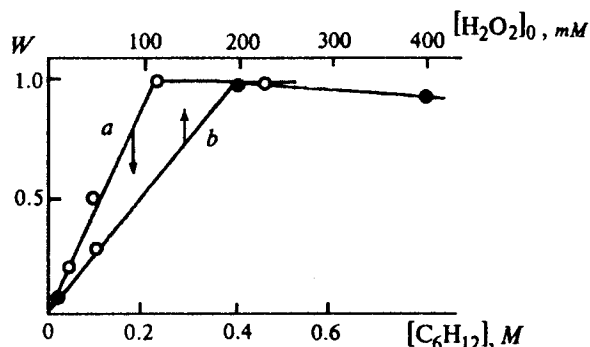


Fig. 2. Dependences of relative initial rates of cyclohexane oxidation W on the initial concentration of cyclohexane (a) and hydrogen peroxide (b). Reaction conditions: 60°C , $10^{-4}\text{ M Bu}_4\text{NVO}_3$ and $4 \cdot 10^{-4}\text{ M PCA}$. a, $[\text{H}_2\text{O}_2]_0 = 0.2\text{ M}$; b, $[\text{C}_6\text{H}_{12}]_0 = 0.464\text{ M}$.

Bu_4NVO_3 , with pyrazine-2-carboxylic acid (PCA) is used as a catalyst. Without PCA, no oxidation takes place. The dependence of the relative initial oxidation rate on the vanadate-PCA ratio is shown in Fig. 1, a. The maximum rate is observed at the $\sim 1:4$ ratio. This ratio was used in all the experiments described below. At sufficiently low catalyst content, the reaction rate is proportional to its concentration (Fig. 1, b), although at $[\text{VO}_3^-] > 10^{-4}\text{ M}$, the reaction rate no longer increases with the rise in concentration of the catalyst. The dependences of reaction rate on the initial concentrations of cyclohexane (Fig. 2, a) and hydrogen peroxide (Fig. 2, b) have similar shapes. The comparison of initial rates of oxidation reaction at various temperatures in the range of $20\text{--}70^\circ\text{C}$ led to an effective activation energy of 76 kJ/mol . On the basis of experiments with perdeuterated cyclohexane, the kinetic isotope effect for the oxidation of this hydrocarbon was calculated to be ~ 1.2 at 50°C .

As noted in the experimental section, the oxidation products of cyclohexane were analyzed by means of GLC. If the reaction solution was injected in the chromatograph without preliminary treatment, the formation of cyclohexanol and cyclohexanone in approximately equal amounts was detected. It should be emphasized that neither product can be formed in substantial amounts from cyclohexane and H_2O_2 directly in the injector or the chromatographic column since in the initial moment of the reaction, when the concentrations of both starting reagents are high, GLC detects only minor quantities of the oxidation products.

If excess triphenylphosphine is added to the reaction solution 10–20 min before the GLC analysis, the resulting chromatogram differs drastically from that of a sample not subjected to reduction by PPh_3 : the cyclohexanol peak rises markedly, while the intensity of the cyclohexanone peak decreases. The sum of alcohol and ketone concentrations in the reduced sample is therefore approximately equal to the total concentration of products in the solution untreated with PPh_3 . The results

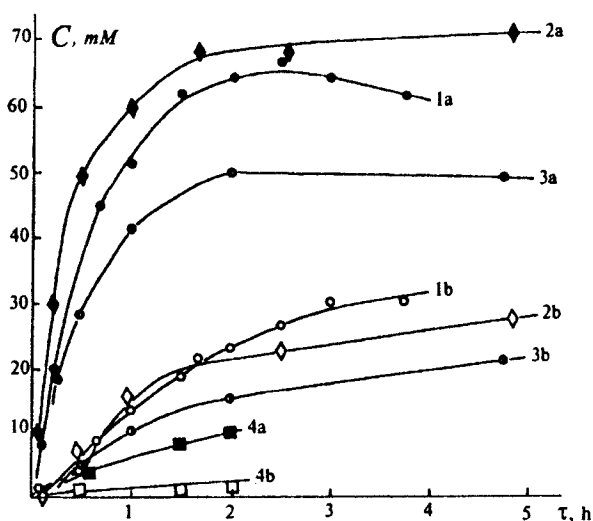


Fig. 3. Kinetic curves of cyclohexyl hydroperoxide (a) and cyclohexanol+cyclohexanone (b) accumulation in reaction of oxidation of cyclohexane (0.23 M) by H_2O_2 (0.2 M) in CH_3CN at 50°C under catalysis by Bu_4NVO_3 (0.1 mM) and PCA (0.4 mM): 1, without admixtures; 2, with 0.01 M of 2,6-di(*tert*-butyl)-4-methylphenol; 3, in the presence of 0.1 M 2-propanol; 4, in the presence of 1.23 M CCl_4 .

obtained can be explained by the fact that on interaction of the reagent described in the present work with cyclohexane, the latter is oxidized mainly to yield cyclohexyl hydroperoxide. As shown in,³³ cyclohexyl hydroperoxide is totally decomposed in the chromatograph to form cyclohexanol and cyclohexanone in the ratio ~1:1. Furthermore, the peroxide is readily and quantitatively reduced by triphenylphosphine to give cyclohexanol.³³ Thus, by comparing the results of chromatographic analysis of the reaction solution before and after reduction by triphenylphosphine, the quantities of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone present in a solution at a given moment can be assessed.

The temperature influences not only the oxidation rate of cyclohexane but also the composition of the products formed. Thus, at 50°C the accumulation of oxidation products terminates in 2 h (Fig. 3a) and the ratio of cyclohexanol to cyclohexanone in the solution reduced by triphenylphosphine equals 6.3. The reaction proceeds even more rapidly at 70°C : in 45 min the concentrations of the alcohol and ketone in the reduced solution reach $63.1 \cdot 10^{-3}$ and $15.4 \cdot 10^{-3}$ M, respectively, i.e. their ratio is 4.1. In both cases cyclohexyl hydroperoxide seems to be the main product that decomposes as the reaction proceeds, forming the alcohol and ketone, with the peroxide decomposition accelerating as the temperature rises. In fact, the maximum concentrations of oxidation products are reached only in 75 h at 20°C (after reduction: $85.1 \cdot 10^{-3}$ and $7.3 \cdot 10^{-3}$ M alcohol and ketone, respectively), thus, a high cyclohexanol to cyclohexanone ratio (11.7) is observed. In this case the concentration of alkyl peroxide is $\sim 70 \cdot 10^{-3}$ M and that of

Table 1. Oxidation of alkanes by H_2O_2 in CH_3CN catalyzed by the $\text{Bu}_4\text{NVO}_3\text{--PCA}$ system¹

Alkane	Concentrations of products ² , mM		Selectivity ³
	Alcohols	Ketones and aldehydes	
<i>n</i> -Hexane	25.2	5.7	C(1):C(2):C(3) = 1:8:7
<i>n</i> -Heptane	22.9	6.0	C(1):C(2):C(3+4) = 1:9:7
2-Methylhexane	23.2	4.8	1°:2°:3° = 1:6:24
3-Methylhexane	15.0	4.5	1°:2°:3° = 1:14:64

¹The reaction was carried out at 50°C for 2 h with 0.23 M alkane, 0.2 M H_2O_2 , 0.1 mM Bu_4NVO_3 , and 0.4 mM PCA.

²The total concentrations of all isomers are listed as determined by GLC after addition of PPh_3 to the reaction solution.

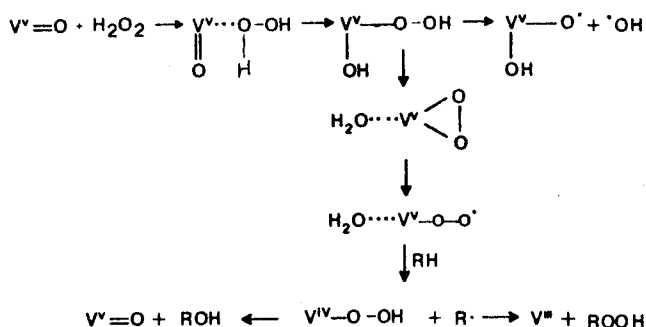
³The relative reactivities of hydrogen atoms at carbon atoms 1, 2, 3 and 4 of linear alkanes and at the primary, secondary, and tertiary carbon atoms of branched alkanes are listed, taking into account the number of hydrogen atoms at each of the carbon atoms.

the alcohol and ketone (in total) is as low as $\sim 15 \cdot 10^{-3}$ M. At this temperature, the highest yield of oxidation products was obtained as calculated with respect to hydrogen peroxide (46% if it is assumed that one H_2O_2 molecule is required to form one alkyl peroxide molecule, while the catalyst turnover number equals 920).

The reagent described effectively oxidizes other alkanes as well. Table 1 presents data on oxidation of certain linear and branched saturated C_6 and C_7 hydrocarbons. It is noteworthy that in this case the experiments were carried out in order to determine the regioselectivity of the process, so the maximum yields of the products were not reached. Like cyclohexane, linear alkanes are oxidized to form appreciable amounts of alkyl peroxides.

This reagent oxidizes benzene to form phenol. Thus, with 1.0 M benzene and 0.2 M H_2O_2 , the concentration of phenol formed at 50°C in 2 h is $2 \cdot 10^{-2}$ M, then its accumulation terminates. Oxidation of toluene produces benzaldehyde along with a mixture of cresol isomers with an *o:m:p* ratio of 54:12:34. In addition to the products of hydroxylation of the aromatic nucleus, 1-phenylethanol ($9.7 \cdot 10^{-3}$ M), acetophenone ($2.5 \cdot 10^{-3}$ M) and 2-phenylethanol ($0.8 \cdot 10^{-3}$ M) are formed in 6 h at 60°C from 0.1 M ethyl benzene (the identification was done after the addition of PPh_3). It is of interest that GLC detected minor quantities of styrene oxide and benzaldehyde as well. Cumene (0.18 M) produces 2-phenyl-2-propanol ($7.7 \cdot 10^{-3}$ M) and acetophenone ($1.1 \cdot 10^{-3}$ M) as the oxidation products of the side chain. Preliminary results also show that under the action of the reagent, cyclohexene undergoes oxygenation primarily into the allylic position.

Scheme



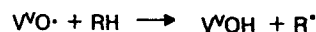
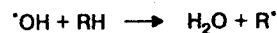
In considering the oxygenation mechanism, one can suppose that the interaction of the VO_3^- -PCA system with H_2O_2 produces hydroxyl radicals, much like ions of iron,³⁴⁻³⁶ copper,^{37,38} and chromium(VI) oxocomplexes.³⁹ Vanadium compounds are known to take part in formation of HO^{\cdot} radicals from O_2 or H_2O_2 in biological systems.^{40,41} In fact, the selectivity parameters for oxygenation of alkanes by the presented reagent listed in the table are close to those determined by us for oxygenation of hydrocarbons by hydroxyl radicals that are formed on action of UV light upon H_2O_2 in CH_3CN . Thus, for *n*-hexane the $\text{C}^1:\text{C}^2:\text{C}^3$ selectivity is 1:10:7. The $1^{\circ}:2^{\circ}:3^{\circ}$ selectivities (i.e., the relative reactivity at the primary, secondary and tertiary carbon atoms) for photochemical oxidation of 2- and 3-methylhexanes by hydrogen peroxide in CH_3CN are 1:6:20 and 1:4:12, respectively. The ψ parameters (i.e. the reactivity of the CH_2 group in ethyl benzene as compared to that in cyclohexane) for reaction of hydrogen peroxide catalyzed by vanadium complex and proceeding under UV irradiation equal 0.5 and 0.8, respectively. It is to be noted that although the selectivity parameters for the reaction with hydroxyl radicals formed by H_2O_2 photolysis and the reaction proceeding catalyzed by the vanadium complex are close, they are not exactly the same. In a similar way, these parameters (for 3-methylhexane oxidation, $1^{\circ}:2^{\circ}:3^{\circ} = 1:7:90$ and $\psi = 1.6$) determined by us⁴² for a stoichiometric reaction with $\text{VO}(\text{O}_2)\text{L}\cdot 2\text{H}_2\text{O}$ peroxide vanadium complex (L denotes 2-picoline)³⁰ are somewhat different from those found for both reactions with the participation of H_2O_2 .

It may be proposed on this basis that in a reaction catalyzed by the vanadium complex, the key role is played by radicals and radical-like species where an unpaired electron is localized on an oxygen atom; primarily hydroxyl radicals. The nascent HO^{\cdot} radicals can attack a hydrocarbon molecule when the former are in the vanadium complex coordination sphere, which naturally leads to somewhat different selectivity as compared to the reaction where real free radicals take part.

A possible mechanism for generation of OH^{\cdot} radicals is shown in the scheme. The hydroxyl radicals are generated in the homolytic rupture of O-O bonds in the

hydroperoxide compound of vanadium. Formation of at least two vanadium-containing species with their unpaired electrons localized on the oxygen atoms (see the scheme) is also possible in this process. The formation of the $\text{V}^{\text{IV}}-\text{O}-\text{O}^{\cdot}$ particle has been postulated earlier.³⁰

Hydroxyl radicals as well as $\text{V}^{\text{V}}-\text{O}^{\cdot}$ and $\text{V}^{\text{IV}}-\text{OO}^{\cdot}$ species abstract a hydrogen atom from the alkane (RH) with generation of an alkyl radical R^{\cdot} capable of reacting rapidly with an oxygen molecule:



ROO^{\cdot} radicals can either interact with hydrogen donors or with a reducing agent and a proton to give a hydroperoxide ROOH , or disproportionate to form molecular oxygen, an alcohol, and a ketone. It has been assumed in³⁰ that $\text{V}^{\text{IV}}-\text{OOH}$ and R^{\cdot} species can interact with formation of ROH and an oxo-derivative of vanadium(V). The possibility for abstraction of the $\cdot\text{OOH}$ group from the vanadium atom by radical R^{\cdot} , as assumed earlier for a reaction with an iron complex,⁴³ must not be ruled out either. An alkyl hydroperoxide should be formed in this case (see the scheme).

Thus, all the reaction paths discussed above can lead to formation of an alkyl hydroperoxide, a ketone, and an alcohol, i.e. products that we have identified in the reaction mixture. The selectivities for reactions catalyzed by the vanadium complex are typical for the processes when a hydrogen atom is abstracted by oxygen-containing radical species. As for certain variation in the values mentioned above, these can be caused by different contribution of several paths to the formation of oxygenation products in the light-stimulated or catalyzed reactions of H_2O_2 , as well as in the stoichiometric reaction with the peroxide complex.

It should be noted that if hydrogen peroxide as an oxidizer is replaced for alkyl hydroperoxide, then the generation of radical species shown in the scheme becomes impossible. In fact, we could detect no products of cyclohexane oxygenation by *tert*-butyl hydroperoxide (used as a 70% aqueous solution).

In the case of oxidation of arenes, the first reaction step consists in addition of a hydroxyl radical or a vanadium-containing radical species to the aromatic nucleus (see²⁶). In contrast to reactions with alkanes, molecular oxygen does not participate directly in oxygenation, hence the yield of oxidation products of arenes is lower. It is of interest that molecular oxygen takes part in the oxidation of alkanes by H_2O_2 in Gif systems⁴⁴ to produce alkyl hydroperoxides,⁴⁵ while addition of chelating amino acids drastically accelerates the oxidation.¹⁸ For oxidation of cyclohexyl hydroperoxide by molecular oxygen in the presence of a vanadium derivative, O_2

activation in [VO-OOR]²⁺ complex has been shown to occur.⁴⁶

Addition of inhibitors of free-radical reactions such as 2,6-di(*tert*-butyl)-4-methylphenol and 2-propanol does not significantly lower the oxidation rate of alkanes (Fig.3). However, on addition of CCl₄ or CBr₄ that react readily with alkyl radicals, the oxygenation rate changes dramatically (Fig.3). Thus the contribution of the chain radical path with abstraction of a hydrogen atom from RH by ROO· as the key stage, seems to be minor. However, an additional detailed study is required to obtain a clearer insight into the mechanism of action of the reagent described in the present paper.

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