

Oxidations by the reagent “O₂–H₂O₂–vanadium derivative–pyrazine-2-carboxylic acid”[☆]

Part 14. Competitive oxidation of alkanes and acetonitrile (solvent)

Yuriy N. Kozlov, Galina V. Nizova, Georgiy B. Shul'pin*

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

Received 10 July 2004; received in revised form 29 October 2004; accepted 30 October 2004

Available online 8 December 2004

Abstract

It has been found that the rate of hydrogen peroxide consumption in an alkane oxidation by the “O₂–H₂O₂–*n*Bu₄NVO₃–pyrazine-2-carboxylic acid” reagent in acetonitrile is noticeably lower in the presence of an alkane than in its absence. This paradoxical phenomenon at the first glance can be explained if we assume that acetonitrile used as a solvent is efficiently oxidized by the system in the absence of alkane. This oxidation is depressed by alkane additive due to the competition between the alkane and acetonitrile for the active hydroxyl radicals efficiently generated by the reagent. It has been also shown that the H₂O₂ decomposition in the presence of an alkane occurs as a radical non-chain process.

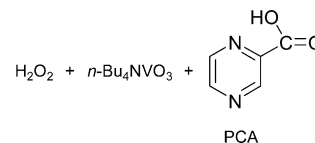
© 2004 Elsevier B.V. All rights reserved.

Keywords: Acetonitrile; Alkanes; Alkyl hydroperoxides; Cyclohexane; Homogeneous catalysis; Methane; Oxidation; Vanadium complexes

1. Introduction

Vanadium complexes are known to catalyze various oxidations of organic compounds including alkanes (see, for example, reviews [1–7] and recent original publications [8–22]). Earlier we have discovered a very efficient reagent for oxidation of organic compounds, especially for hydroperoxidation of saturated hydrocarbons [23–36]. This reagent based on atmospheric oxygen as oxidant and hydrogen peroxide as a promoter of the oxidation as well as a combination of *n*-tetrabutylammonium vanadate (or any other vanadium derivative) and pyrazine-2-carboxylic acid (PCA) as a catalyst oxidizes alkanes predominantly to the corresponding alkyl hydroperoxides. Alkyl hydroperoxides are partially de-

composed in the course of the reaction to the more stable ketones and alcohols.



Usually acetonitrile has been used as a solvent. The oxidative ability of the “O₂–H₂O₂–V complex–PCA” reagent is due to the hydroxyl radical formation in the hydrogen peroxide decomposition. The oxidation is induced by the attack of hydroxyl radical on the alkane, RH, to produce alkyl radicals, R•. The latter further rapidly react with molecular atmospheric oxygen. Peroxyl radicals, ROO•, thus formed can be converted to alkyl hydroperoxides. The rate-limiting step of the reaction [35] is the monomolecular decomposition of the complex containing one coordinated PCA molecule:



[☆] For parts 1–13, see [24–36], respectively

* Corresponding author. Tel.: +7 095 939 7317; fax: +7 095 137 6130.
E-mail address: shulpin@chph.ras.ru (G.B. Shul'pin).

The V(IV) species thus formed reacts further with the second H₂O₂ molecule to generate the hydroxyl radical according to the following equation:



It has been assumed that the accelerating role of PCA is ascribed to the facilitation of the proton transfer between oxo and hydroxy ligands of vanadium complex on the one hand, and molecules of hydrogen peroxide and water on the other hand (“a robot’s arm mechanism”) [35].

The efficiency of the H₂O₂ usage in the oxidations by this reagent is less than 100% especially in the case of relatively inert alkanes used as substrates. Indeed, one can a priori assume that some amount of hydrogen peroxide will be decomposed “non-productively” to afford molecular oxygen (“catalase activity” of the catalyst) and H₂O₂ might be also consumed for the oxidation of the solvent (acetonitrile). In the present work we investigated the alkane oxidation by the “O₂–H₂O₂–V complex–PCA” reagent taking into account the aspect of the productivity of H₂O₂ usage.

2. Experimental

Aqueous “35% hydrogen peroxide solution” (“Fluka”, stabilized, a solution in water with concentration 11.5 mol dm⁻³, or 38%, determined by the titration) was used as received. The experiments on alkane oxidations were carried out in water in thermostated Pyrex cylindrical vessels (total volume 10 mL) with vigorous stirring. The total volume of the reaction mixture was usually 2–5 mL. In a typical experiment, initially, a portion of the aqueous solution of H₂O₂ was added to the solution of the alkane, catalyst (*n*-tetrabutylammonium vanadate) and co-catalyst (PCA).

In order to determine concentrations of all cyclohexane oxidation products the samples of reaction solutions were in some cases analyzed twice (before and after their treatment with PPh₃) by GC (LKhM-80-6 instrument, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) to measure concentrations of cyclohexanol and cyclohexanone. This method (an excess of solid triphenylphosphine is added to the samples 10–15 min before the GC analysis) [4–6] allows us to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding alcohol and ketone. Nevertheless, in our kinetic studies described below, we measured concentrations of cyclohexanone and cyclohexanol only after reduction of the reaction mixture with PPh₃ which gives precisely concentration of a sum of the oxygenates. This total concentration is used for measuring the reaction rates.

Current concentration of H₂O₂ was determined spectrophotometrically after addition of titanium(IV) sulfate [37]. In experiments involving molecular oxygen evolution, the volume of dioxygen evolved was measured using a thermostated burette. The reaction system was connected to a manometric burette with water, which was saturated with air prior to use. After certain time intervals, the pressure was equilibrated using a separation funnel by adjusting the water level to the same heights. Synthesis of *n*-Bu₄NVO₃ is described in the literature [35,38].

3. Results

In this work we studied for the first time the consumption of hydrogen peroxide and dioxygen evolution in the presence and absence of an alkane. In our previous publications [24–36], we described only the formation of alkyl hydroperoxides from alkanes under the action of the reagent. We have found that in the presence of vanadate anion and PCA, hydrogen peroxide in acetonitrile at 50 °C decomposes to evolve molecular oxygen; however, the stoichiometry is in accordance with expression (C):



If PCA is used in excess compared with the vanadium concentration, the rate of the dioxygen evolution is proportional to the initial concentration of the vanadate anion (Fig. 1).

The dependences of the reaction rate on the initial concentration of hydrogen peroxide are presented in Fig. 2. Comparison of graphs A and B clearly shows that hydrogen peroxide decomposition to O₂ is noticeably more rapid if cyclohexane is not present in the reaction solution. The second feature of this reaction is the higher rate of H₂O₂ consumption in comparison with O₂ accumulation in the absence of cyclohexane.

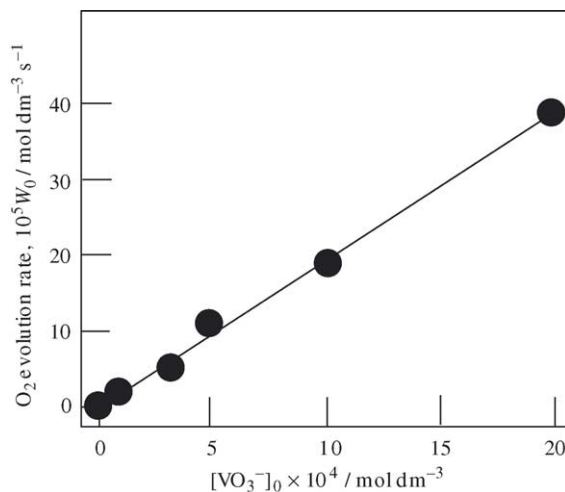


Fig. 1. Plot of initial rate of dioxygen evolution in the H₂O₂ decomposition in MeCN vs. initial concentration of *n*-Bu₄NVO₃. Conditions: [H₂O₂]₀ = 0.96 mol dm⁻³; [PCA]₀ = 25 × 10⁻⁴ mol dm⁻³; 50 °C.

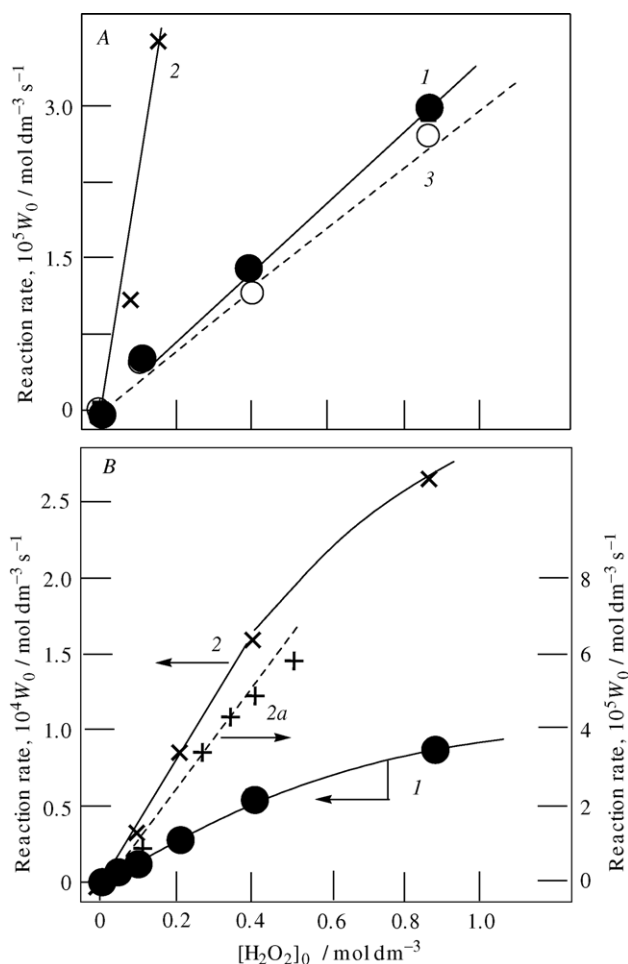


Fig. 2. Decomposition of H_2O_2 in MeCN at 50°C . Dependences of initial rates of O_2 evolution (curves 1), H_2O_2 consumption (curves 2) and cyclohexane oxygenates formation (curve 3) on initial concentration hydrogen peroxide are shown. Conditions: $[n\text{-Bu}_4\text{NVO}_3]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{PCA}]_0 = 25 \times 10^{-4} \text{ mol dm}^{-3}$. Hydrogen peroxide was added as 35% aqueous solution. Graph A: the reaction in the presence of cyclohexane (0.46 mol dm^{-3}); graph B: the reaction in the absence of cyclohexane. Curve 2a was obtained for the reaction when additional water was added in order to even the influence of water from the hydrogen peroxide sample.

Both dependences testify the first order in respect to H_2O_2 at its relatively low concentrations.

In the absence of PCA almost no O_2 evolution can be noticed. At $[\text{PCA}] < 10 \times 10^{-4} \text{ mol dm}^{-3}$ the O_2 evolution rate increases linearly with growth of $[\text{PCA}]$ and at $[\text{PCA}] > 10 \times 10^{-4} \text{ mol dm}^{-3}$ does not grow with rise of $[\text{PCA}]$ (Fig. 3). Moreover, maximum can be noticed at $[\text{PCA}] \approx (10/20) \times 10^{-4} \text{ mol dm}^{-3}$. It is interesting that picolinic acid also accelerates the O_2 evolution with a much more sharp maximum at approximately $8 \times 10^{-4} \text{ mol dm}^{-3}$ (see Fig. 3, curve 2).

We determined efficient activation energy of the O_2 evolution (Fig. 4), which turned out to be approximately equal (20 kcal mol^{-1}) to that for the cyclohexane hydroperoxidation (17 kcal mol^{-1}) [35] or benzene hydroxylation (19 kcal mol^{-1}) [36]. Phenol taken in relatively large ex-

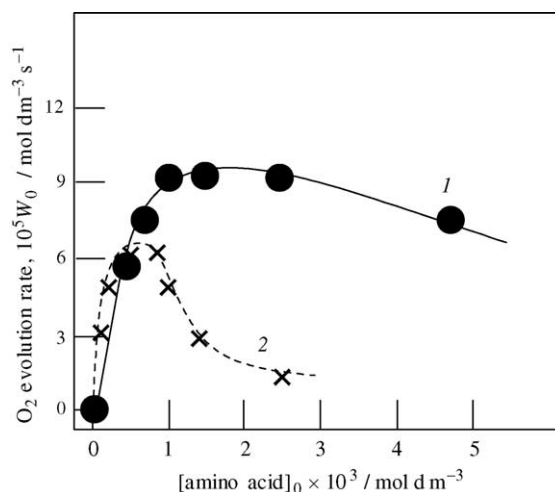


Fig. 3. Plots of initial rate of dioxygen evolution in the H_2O_2 decomposition in MeCN vs. initial concentration of added PCA (curve 1) or picolinic acid (curve 2). Conditions: $[n\text{-Bu}_4\text{NVO}_3]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[H_2O_2]_0 = 0.96 \text{ mol dm}^{-3}$; 50°C .

cess to the vanadium ion decreases the O_2 evolution rate, whereas 2,6-dimethyl-4-*tert*-butylphenol containing a sterically shielded OH group almost does not affect the rate (Fig. 5).

4. Discussion

It is known that in aqueous solution reactions of photochemical hydrogen peroxide decomposition as well as its decomposition under the action of ions and complexes of transition metals occurs as radical chain processes [39–41]. Chain transfer agents in these reactions are inter alia hydroxyl (HO^\bullet) and hydroperoxyl (HO_2^\bullet) radicals. Chain propagation

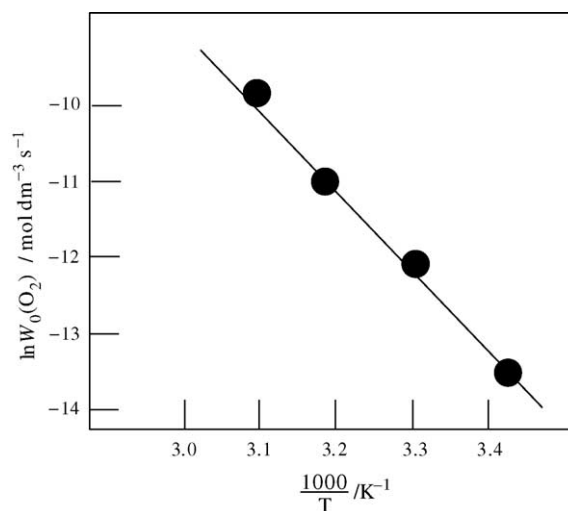


Fig. 4. Dependence of the initial dioxygen evolution rate on temperature in the H_2O_2 decomposition in MeCN which corresponds to $E_a = 20 \text{ kcal mol}^{-1}$. Conditions: $[n\text{-Bu}_4\text{NVO}_3]_0 = 1 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{PCA}]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[H_2O_2]_0 = 0.96 \text{ mol dm}^{-3}$.

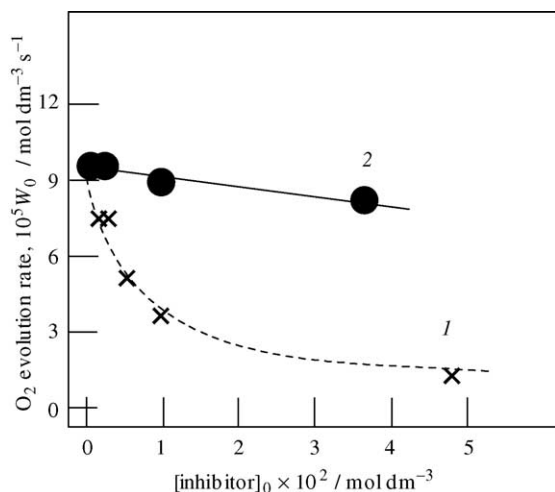
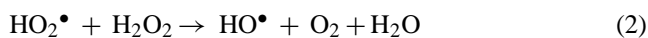
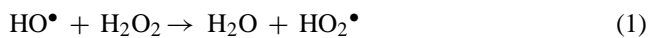
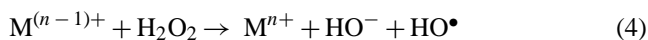
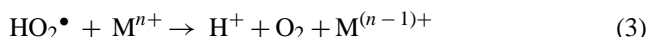


Fig. 5. Plots of initial rate of dioxygen evolution in the H_2O_2 decomposition in MeCN vs. initial concentration of added phenol (curve 1) or 2,6-dimethyl-4-*tert*-butylphenol (curve 2). Conditions: $[\textit{n}\text{-Bu}_4\text{NVO}_3]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{PCA}]_0 = 25 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{O}_2]_0 = 0.96 \text{ mol dm}^{-3}$; 50°C .

stages in the photochemical process are the following reactions:



In addition to the participation in the chain initiation stage, transition metal ions M^{n+} usually catalyze stage (2) in accordance with the following scheme:



Certain organic substances, when added to these systems do not change the initiation rate but decrease the decomposition rate of hydrogen peroxide. A decrease in the decomposition rate of hydrogen peroxide is due to the change of the mechanism of the chain termination because the interaction between hydroxyl radicals and the organic substance leads to the formation of secondary radicals which are less reactive in the propagation stage but efficient in the chain termination step. Efficiency in the suppression of the chain process should depend on the reactivity of the secondary radicals. Only in the case when these radicals are inactive in the chain termination step, the whole chain process is completely suppressed and the oxidation rate of the organic substance equals to the initiation rate. In the aqueous solution, the inhibition of the hydrogen peroxide decomposition occurs usually when concentration of the organic compound is much less than hydrogen peroxide concentration. This fact is due to the higher reactivity of organic compounds towards hydroxyl radicals in comparison with the reactivity of H_2O_2 , as well as the chain mechanism of the H_2O_2 decomposition.

It is clear that in an organic solvent, chain processes of hydrogen peroxide decomposition will be accompanied

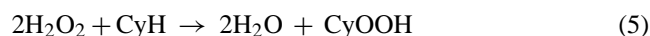
with conjugated solvent oxidation reactions because solvent molecules usually react with hydroxyl radicals. The same can be said about radical chain processes of organic peroxide decomposition and about any radical process in which generated free radicals react with solvent molecules.

It follows from Fig. 2 that the initial rate of hydrogen peroxide decomposition (at its initial concentration 0.5 mol dm^{-3}) at 50°C in the presence of catalyst *n*- Bu_4NVO_3 ($5 \times 10^{-4} \text{ mol dm}^{-3}$) and co-catalyst PCA ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) is equal to $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Under the same conditions the rate of molecular oxygen evolution is equal to $0.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Thus, it can be concluded that the hydrogen peroxide is consumed for the oxidation of the reaction solution components with the rate of $0.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. The oxidation of the reaction solution components leads to the formation of such products as formaldehyde, carbon monoxide and formic acid [33] with the yields growing with the reaction time. Total yield of these products is however not high, and other possible products have not been identified by us. It can be assumed that two substances PCA and acetonitrile can be potentially oxidized under conditions described above. Taking into account that oxidizing ability of the system under discussion is due to the hydroxyl radical generation, we can propose that acetonitrile will be mainly oxidized. Indeed if for the interaction between PCA and HO^\bullet we assume the rate constant to be equal to $1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, we will calculate that the rate ratio for the HO^\bullet interactions with PCA and CH_3CN is not higher than 0.07 (at $[\text{PCA}] = 2.5 \text{ mol dm}^{-3}$ and $[\text{CH}_3\text{CN}] = 17 \text{ mol dm}^{-3}$), because $k(\text{HO}^\bullet + \text{CH}_3\text{CN}) = 2.2 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [42]. In reality, however, $k(\text{HO}^\bullet + \text{PCA})$ should be lower than $1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

This assumption is supported by two experimental results described below. If we would assume that a compound, which is mainly oxidized is PCA, we will need to accept that the typical time of the added PCA ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) consumption might be ca. 2.5 min because the rate of hydroxyl radical generation under our conditions is higher than $1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ (see below). Consequently, during this time, in accordance with the data of Fig. 3, a substantial catalyst deactivation could occur, which is in contradiction with our experimental results. Secondly, if we assume that PCA is a substance, which is mainly oxidized in the system under consideration, we should expect that an increase of PCA concentration (after attaining the maximum rate) would lead to a sharp decrease of the rates of both cyclohexane oxidation and dioxygen evolution. On the contrary, the data of Fig. 3 and results obtained in [40] demonstrate that the effects of [PCA] on the reaction rates at $[\text{PCA}] > 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ are negligible.

Previously analyzing the dependence of the rate of cyclohexyl hydroperoxide formation on the initial cyclohexane concentration [35], we took into account the possibility of hydroxyl radical to be accepted by acetonitrile. This analysis was based on the assumption that cyclohexane does

not affect the hydroxyl radical generation rate. Moreover, we assumed that secondary radicals generated from both cyclohexane and acetonitrile do not take part in the chain hydrogen peroxide decomposition with participation of hydroxyl radicals. A conclusion was made from this analysis that when cyclohexane concentration is high, the rate of cyclohexyl hydroperoxide formation approaches the rate of hydroxyl radical generation by this system that is the initiation rate. If this assumption is true, the cyclohexane additives should not affect the hydrogen peroxide decomposition rate. However, our experiments unexpectedly demonstrated that under the conditions described above cyclohexane added to the reaction solution decreases the rate of hydrogen peroxide decomposition. For example, in the presence of 0.46 dm^{-3} of cyclohexane and $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mol dm}^{-3}$ the rates of H_2O_2 decomposition and O_2 evolution dropped to 0.9×10^{-4} and $0.15 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively, from the initial rates 2×10^{-4} and $0.6 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ obtained in the absence of cyclohexane (see Fig. 2). The rate of the formation of the main oxidation product cyclohexyl hydroperoxide is equal to $0.15 \times 10^{-4} \text{ mol dm}^3 \text{ s}^{-1}$, that is 70% of the initiation rate [35,43]. Experimentally found kinetic features of the process are the following. On growing initial concentration of added cyclohexane (CyH), the dioxygen evolution rate approaches zero and the hydrogen peroxide decomposition rate approaches a two-fold rate of cyclohexyl hydroperoxide (CyOOH) formation. Thus, total reaction of the catalytic cyclohexane oxidation corresponds to the following equation:



The obtained experimental data show that in the absence of the cyclohexane each hydroxyl radical generated by the catalytic system induces the decomposition of 10 molecules of hydrogen peroxide and approximately half of these molecules is used for the acetonitrile oxidation, whereas, the other half of molecules is consumed for the H_2O_2 decomposition leading to the formation of molecular oxygen. Since the rate constants of hydroxyl radical interactions with the acetonitrile and H_2O_2 are close [42] and concentration of the acetonitrile is much higher than hydrogen peroxide concentration, all induced HO^\bullet radicals will react with CH_3CN (for the reactions of hydrogen peroxide with acetonitrile, see, for example, [33,44,45]).

It is important to note that the additional consumption of hydrogen peroxide in the acetonitrile oxidation induced by radicals formed from the acetonitrile cannot be due to a radical chain process of the hydrogen peroxide decomposition with the formation of hydroxyl radicals. An assumption that radicals generated in the interaction between CH_3CN and HO^\bullet induce the chain process of hydrogen peroxide decomposition with the formation of hydroxyl radicals is in contradiction, first of all with the main thesis accepted in [35]. This thesis describes a competitive interaction of acetonitrile and cyclohexane with hydroxyl radicals. A model proposed

in [35] which does take into account reactions of secondary radicals nevertheless quantitatively describes the experimental data. However, if we accept that radicals formed from the acetonitrile can induce a chain process of the H_2O_2 decomposition, we will find that, stationary concentration of hydroxyl radicals is higher than in the absence of the interaction between secondary radicals formed from CH_3CN and H_2O_2 , due to the additional generation of hydroxyl radicals in the cycle of H_2O_2 decomposition. As a result efficiency of the acetonitrile on the yield of cyclohexyl hydroperoxide should be less than that expected on the basis of radiochemical experiments giving rate constants of the interaction between hydroxyl radicals with either acetonitrile or cyclohexane. It means that experimentally measured ratio

$$\frac{k(\text{HO}^\bullet + \text{CH}_3\text{CN})}{k(\text{HO}^\bullet + \text{CyH})} \quad (6)$$

should be less than the corresponding calculated ratio.

Further, we might expect some difference in the values of the ratio (6) measured in photochemical (in the absence of a catalyst) [43] and in catalytic (in the presence of a catalyst) experiments, because the participation of the catalyst in the cycle of the chain propagation is very probable. Thirdly, the experimental dependence of the cyclohexyl hydroperoxide formation rate on cyclohexane concentration should not generally correspond to the dependence, which can be predicted by the simple competitive scheme [35]. We have found that in reality the constant ratio is in concordance with the ratio calculated from the radiolysis data. As this ratio is practically the same for both photochemical and catalytic experiments [43], we can state that the experimental data are in agreement with the simple competitive scheme. This is why we propose that the additional consumption of hydrogen peroxide for terminal products is not due to the chain H_2O_2 decomposition (which occurs via the generation of hydroxyl radicals), and that this decomposition is not induced by radicals formed from acetonitrile.

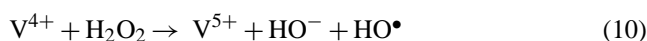
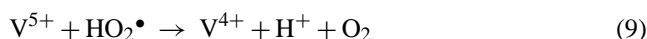
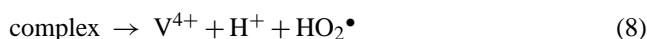
The catalytic H_2O_2 decomposition under the action of vanadate ions is not a radical chain but a radical process, because in acetonitrile the rate of potentially possible chain termination stage (1) is much lower than the rate of the interaction between hydroxyl radicals and acetonitrile (i.e., the chain termination rate). We assume that the main route leading to the dioxygen evolution is due to the secondary processes of acetonitrile oxidation by hydrogen peroxide. Indeed the O_2 evolution rate decreases with decreasing acetonitrile oxidation rate. Under studied conditions ($[\text{n-Bu}_4\text{NVO}_3] = 5 \times 10^{-4}$, $[\text{PCA}] = 2.5 \times 10^{-3}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol dm}^{-3}$ and 50°C) in the absence of added cyclohexane, we detected a large hydrogen peroxide consumption per one hydroxyl radical inducing the oxidation in our catalytic system. Additives of cyclohexane lead to the substantial decrease of H_2O_2 consumption, and a goal product is formed, CyOOH: see Table 1 which contains rates of cyclohexane oxidation, $W(\text{CyH})$, and hydrogen peroxide consumption, $W(\text{H}_2\text{O}_2)$, at various initial concentrations of

Table 1
Rates of H₂O₂ decomposition and CyH oxygenation at various initial CyH concentrations

[CyH] ₀ (mol dm ⁻³)	10 ⁴ × W(H ₂ O ₂) (mol dm ⁻³ s ⁻¹)	10 ⁴ × W(CyH) (mol dm ⁻³ s ⁻¹)
0	2.0	0
0.46	0.9	0.15
0.92	0.7	0.175
1.84	0.6	0.19

cyclohexane. The data from Table 1 show, for example, that at [CyH] = 0.92 mol dm⁻³ and when 38% aqueous H₂O₂ is used approximately a half of all hydrogen peroxide amount is consumed for the cyclohexane oxidation, whereas, the second half of H₂O₂ is used for the acetonitrile oxidation and dioxygen formation.

When cyclohexane is present in a high concentration, acetonitrile as an acceptor of hydroxyl radicals affects neither hydrogen peroxide decomposition rate nor cyclohexane oxidation rate. Taking into account the stoichiometry of the cyclohexane oxidation, Eq. (5), and the fact previously described by us that CyOOH is not formed if a stream of argon is bubbled through the reaction solution [35] we can propose that dioxygen necessary for the reaction (a catalytic cycle, see [35]) is formed in appropriate amount during the H₂O₂ decomposition in the catalytic cycle. Based on this statement we propose the following mechanism of the H₂O₂ decomposition and the simultaneous cyclohexane oxidation at relatively high concentration of the latter when all generated hydroxyl radicals react with the alkane:



We have found that other alkanes (*n*-heptane and 2,2,4-trimethylpentane) affect the process in an analogous manner. These hydrocarbons added to the reaction solution depress the cyclohexane oxidation process and the initial rate of CyH oxidation is approximately three times as low as that in the absence of the additive. The effect of the second hydrocarbon additive on the CyOOH yield can be described by a simple competitive scheme, which assumes that secondary radicals do not take part in the hydrogen peroxide decomposition. The analysis of our experimental data allowed us to measure the ratio of rate constants:

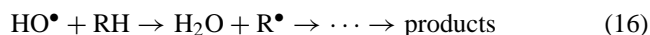
$$\frac{k(\text{HO}^\bullet + 2, 2, 4\text{-trimethylpentane})}{k(\text{HO}^\bullet + \text{cyclohexane})} = 1.16 \pm 0.06 \quad (14)$$

This parameter is in good agreement with the value (1.15) calculated on the basis of radiolysis experiments [42].

Added methanol decreases the hydrogen peroxide decomposition rate to much less extent in comparison with the alkanes. For example, at [MeOH] = 0.5 mol dm⁻³ the value of W(H₂O₂) is only by 30% lower than in the absence of methanol. This is not due to the difference between rate constants for the reaction of hydroxyl radicals with methanol and cyclohexane. Indeed, rate constants for oxidations of both substrates are very similar: $(8.4 \pm 1.7) \times 10^8$ and $1.25 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. Less efficient decrease in the H₂O₂ decomposition rate in the case of methanol, when compared with alkanes can be explained if we accept that radicals formed from methanol induce the chain process of the H₂O₂ decomposition with participation of hydroxyl radicals, as shown in Eqs. (1) and (2). Such a route is impossible in the case of alkanes.

5. Conclusions

In this work we followed the alkane, RH, oxidation with the “O₂-H₂O₂-*n*Bu₄NVO₃-PCA” reagent in acetonitrile by measuring the hydrogen peroxide consumption in the course of the reaction and found that the rate of this consumption is noticeably higher in the absence of the alkane. This phenomenon can be understood by introducing the following mechanistic scheme. Hydrogen peroxide generates under the action of the vanadium complex hydroxyl radicals, which competitively react both with MeCN and RH:



Reaction (15) requires larger amount of H₂O₂ in comparison with process (16). Indeed, as the reaction between HO[•] and MeCN generates reactive nitrogen-containing intermediates, which require additional amounts of H₂O₂ for their deep oxidation, in the oxidation of one molecule of MeCN much more than one molecule of hydrogen peroxide is consumed in total. As a result we notice a sharp decrease of the hydrogen peroxide decomposition rate when RH is added to the system and reaction (16) (which needs much less amount of H₂O₂) becomes the predominant process.

Acknowledgments

This work was supported by the grant from the Section of Chemistry and Material Science of the Russian Academy of Sciences (Program “A theoretical and experimental study of chemical bonds and mechanisms of main chemical processes”, Project “The solvent effects in redox processes, which include the electron transfer stages”).

References

- [1] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* 94 (1994) 626–638.
- [2] V. Conte, F. Di Furia, G. Licini, *Appl. Catal. A: General* 157 (1997) 335–361.
- [3] A.E. Shilov, G.B. Shul'pin, *Chem. Rev.* 97 (1997) 2879–2932.
- [4] A.E. Shilov, G.B. Shul'pin, Homogeneous catalytic oxidation of hydrocarbons by peroxides and other oxygen atom donors, in: *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht, 2000 (Chapter 10), pp. 430–465.
- [5] G.B. Shul'pin, *J. Mol. Catal. A: Chem.* 189 (2002) 39–66.
- [6] G.B. Shul'pin, *Comptes Rendus, Chimie* 6 (2003) 163–178.
- [7] G.B. Shul'pin, in: M. Beller, C. Bolm (Eds.), *Transition Metals for Organic Synthesis*, vol. 2, second ed., Wiley–VCH, Weinheim, New York, 2004, pp. 215–242.
- [8] N.A. Alekar, V. Indira, S.B. Halligudi, D. Srinivas, S. Gopinathan, C. Gopinathan, *J. Mol. Catal. A: Chem.* 164 (2000) 181–189.
- [9] J.-M. Brégeault, F. Launay, A. Atlamsani, *Comptes Rendus, Chimie* 4 (2001) 11–26.
- [10] G. Süß-Fink, L. Gonzalez, G.B. Shul'pin, *Appl. Catal. A: General* 217 (2001) 111–117.
- [11] K.P. Bryliakov, E.P. Talsi, T. Kühn, C. Bolm, *New J. Chem.* 27 (2003) 609–614.
- [12] G.S. Mishra, A. Kumar, *React. Kinet. Catal. Lett.* 80 (2003) 223–231.
- [13] K.P. Bryliakov, E.P. Talsi, S.N. Stas'ko, O.A. Kholdeeva, S.A. Popov, A.V. Tkachev, *J. Mol. Catal. A: Chem.* 194 (2003) 79–88.
- [14] M. Vennat, P. Herson, J.-M. Brégeault, G.B. Shul'pin, *Eur. J. Inorg. Chem.* (2003) 908–917.
- [15] G.B. Shul'pin, E.R. Lachter, *J. Mol. Catal. A: Chem.* 197 (2003) 65–71.
- [16] E. Battistel, R. Tassinari, M. Fornaroli, L. Bonoldi, *J. Mol. Catal. A: Chem.* 202 (2003) 107–115.
- [17] J.E. Remias, T.A. Pavlovsky, A. Sen, *J. Mol. Catal. A: Chem.* 203 (2003) 179–192.
- [18] P.M. Reis, J.A.L.A.F. Silva Palavra, J.J.R. Fraústo da Silva, T. Kitamura, Y. Fujiwara, A.J.L. Pombeiro, *Angew. Chem. Int. Ed.* 42 (2003) 821–823.
- [19] S. Seelan, A.K. Sinha, *Appl. Catal. A: General* 238 (2003) 201–209.
- [20] E.D. Park, Y.-S. Hwang, C.W. Lee, J.S. Lee, *Appl. Catal. A: General* 247 (2003) 269–281.
- [21] G.B. Shul'pin, Yu.N. Kozlov, *Org. Biomol. Chem.* 1 (2003) 2302–2306.
- [22] T. Joseph, M. Hartmann, S. Ernst, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 207 (2004) 129–135.
- [23] G.B. Shul'pin, D. Attanasio, L. Suber, *J. Catal.* 142 (1993) 147–152.
- [24] G.B. Shul'pin, D. Attanasio, L. Suber, *Russ. Chem. Bull.* 42 (1993) 55–59.
- [25] G.B. Shul'pin, A.N. Druzhinina, G.V. Nizova, *Russ. Chem. Bull.* 42 (1993) 1327–1329.
- [26] G.V. Nizova, G.B. Shul'pin, *Russ. Chem. Bull.* 43 (1994) 1146–1148.
- [27] G.B. Shul'pin, G. Süß-Fink, *J. Chem. Soc., Perkin Trans. 2* (1995) 1459–1463.
- [28] G.B. Shul'pin, R.S. Drago, M. Gonzalez, *Russ. Chem. Bull.* 45 (1996) 2386–2388.
- [29] M.C. Guerreiro, U. Schuchardt, G.B. Shul'pin, *Russ. Chem. Bull.* 46 (1997) 749–754.
- [30] G.B. Shul'pin, M.C. Guerreiro, U. Schuchardt, *Tetrahedron* 52 (1996) 13051–13062.
- [31] G.V. Nizova, G. Süß-Fink, G.B. Shul'pin, *Tetrahedron* 53 (1997) 3603–3614.
- [32] U. Schuchardt, M.C. Guerreiro, G.B. Shul'pin, *Russ. Chem. Bull.* 47 (1998) 247–252.
- [33] G. Süß-Fink, G.V. Nizova, S. Stanislas, G.B. Shul'pin, *J. Mol. Catal. A: Chem.* 130 (1998) 163–170.
- [34] G.B. Shul'pin, Y. Ishii, S. Sakaguchi, T. Iwahama, *Russ. Chem. Bull.* 48 (1999) 887–890.
- [35] G.B. Shul'pin, Yu.N. Kozlov, G.V. Nizova, G. Süß-Fink, S. Stanislas, A. Kitaygorodskiy, V.S. Kulikova, *J. Chem. Soc., Perkin Trans. 2* (2001) 1351–1371.
- [36] M.H.C. de la Cruz, Yu.N. Kozlov, E.R. Lachter, G.B. Shul'pin, *New J. Chem.* 27 (2003) 634–638.
- [37] G.M. Eisenberg, *Ind. Eng. Chem. Anal. Ed.* 15 (1943) 327.
- [38] V.W. Day, W.G. Klemperer, A. Yagasaki, *Chem. Lett.* (1990) 1267–1268.
- [39] S. Luňák, P. Sedláč, *J. Photochem. Photobiol. A: Chem.* 68 (1992) 1–33.
- [40] A.N. Ermakov, Yu.N. Kozlov, A.P. Purmal', *Kinetika i Kataliz* 40 (1999) 663–675 (in Russian).
- [41] A.Ya. Sychev, G.G. Duka, *Fundamental and Applied Aspects of Homogeneous Catalysis by Metal Complexes. Part 2*, Moldovian State University, Chisinau, 2002, pp. 3–442 (in Russian).
- [42] A.K. Pikaev, S.A. Kabakchi, *Reactivity of Primary Products of Water Radiolysis*, Energoizdat, Moscow, 1982 (in Russian).
- [43] G.B. Shul'pin, G.V. Nizova, Yu.N. Kozlov, L. Gonzalez Cuervo, G. Süß-Fink, *Adv. Synth. Catal.* 346 (2004) 317–332.
- [44] G. Laus, *J. Chem. Soc., Perkin Trans. 2* (2001) 864–868.
- [45] H.-D. Brauer, B. Eilers, A. Lange, *J. Chem. Soc., Perkin Trans. 2* (2002) 1288–1295.