Oxidation of 2-Propanol and Cyclohexane by the Reagent “Hydrogen Peroxide−Vanadate Anion−Pyrazine-2-carboxylic Acid”: Kinetics and Mechanism†

Yuriy N. Kozlov,‡ Vladimir B. Romakh,§ Alex Kitaygorodskiy,⊥ Péter Buglyó,|| Georg Süss-Fink,§ and Georgiy B. Shul’pin*,‡

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia, Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51,CH−2009 Neuchâtel, Switzerland, Chemistry Department, Clemson University, Clemson, South Carolina 29634-0973, and Department of Inorganic and Analytical Chemistry, University of Debrecen, P.O. Box 21, H-4010 Debrecen, Hungary

Received: January 5, 2007

The vanadate anion in the presence of pyrazine-2-carboxylic acid (PCA ≡ pcaH) efficiently catalyzes the oxidation of 2-propanol by hydrogen peroxide to give acetone. UV−vis spectroscopic monitoring of the reaction as well as the kinetics lead to the conclusion that the crucial step of the process is the monomolecular decomposition of a diperoxovanadium(V) complex containing the pca ligand to afford the peroxyl radical, $HOO^\bullet$ and a V(IV) derivative. The rate-limiting step in the overall process may not be this (rapid) decomposition itself but (prior to this step) the slow hydrogen transfer from a coordinated H_2O_2 molecule to the oxygen atom of a pca ligand at the vanadium center: “(pca)(O═)V···O_2H_2” → “(pca)(HO−)V−OOH”. The V(IV) derivative reacts with a new hydrogen peroxide molecule to generate the hydroxyl radical (“V^{IV}” + H_2O_2 → “V^V” + HO^- + $HO^\bullet$), active in the activation of isopropanol: $HO^\bullet + Me_2CH(OH) \rightarrow H_2O + Me_2C^\bullet(OH)$. The reaction with an alkane, RH, in acetonitrile proceeds analogously, and in this case the hydroxyl radical abstracts a hydrogen atom from the alkane: $HO^\bullet + RH \rightarrow H_2O + R^\bullet$. These conclusions are in a good agreement with the results obtained by Bell and co-workers (Khaliullin, R. Z.; Bell, A. T.; Head-Gordon, M. *J. Phys. Chem. B* **2005**, *109*, 17984−17992) who recently carried out a density functional theory study of the mechanism of radical generation in the reagent under discussion in acetonitrile.

1. Introduction

Soluble and supported vanadium complexes are known to efficiently catalyze various oxidative transformations of organic compounds (see reviews[1] and recent original papers[2−8]). Oxo and peroxo derivatives of vanadium play important role in such oxidations.[9]

Earlier we have discovered that the vanadate anion (as well as any other vanadium derivative) efficiently catalyzes the oxidation of organic compounds in acetonitrile, if pyrazine-2-carboxylic acid (PCA ≡ pcaH) is present as a cocatalyst in the solution in low concentrations[10] (see also preliminary communications,[11] reviews,[12] and related papers[13]). On the basis of a kinetic study of the alkane oxidation, we proposed[10l,m,11d,12c,d] a mechanism with two crucial steps: decomposition of a transient peroxovanadium(V) complex to produce a peroxyl radical and a V(IV) derivative (equation A) and further interaction of this V(IV) complex with another hydrogen peroxide molecule to afford hydroxyl radical (equation B) which attacks the hydrocarbon

$$\text{“}V^V\text{−OOH”} \rightarrow \text{“}V^{IV}\text{”} + HOO^\bullet \qquad \text{(A)}$$

$$\text{“}V^{IV}\text{”} + H_2O_2 \rightarrow \text{“}V^V\text{”} + HO^- + HO^\bullet \qquad \text{(B)}$$

Reaction A is a rate-limiting step. We assumed that PCA coordinated to the vanadium center in the form of the pca ligand facilitates the proton transfer between the oxo or hydroxy ligands of the vanadium complex on the one hand and molecules of hydrogen peroxide or water on the other hand, for example

$$\text{“O═V}\cdots O_2H_2\text{”} \rightarrow \text{“HO−V−OOH”} \qquad \text{(C)}$$

We noted that such a “robot’s arm mechanism” may have analogies in enzyme catalysis. (Vanadium is known to promote hydroxyl radical formation in living organisms.[14])

Recently Bell and co-workers[15] studied the mechanism of hydrocarbon oxidation by this reagent using density functional theory (DFT) and found that “the generation of $HOO^\bullet$ radicals cannot occur via cleavage of a V−OOH bond in the complex formed directly from the precursors” because the activation barrier for this process is too high. Instead, peroxyl radicals are formed via a sequence of additional steps, and diperoxo complexes are involved in this transformation. Besides, the conversion of the precursors requires hydrogen transfer from H_2O_2 to a vanadyl group, and the calculations by Bell and co-workers showed “that direct transfer has a higher barrier than pca-assisted indirect transfer. Indirect transfer occurs by migration of hydrogen from coordinated H_2O_2 to the oxygen of a pca ligand connected to the vanadium atom”.[15]

[†] This is part 16 of the series “Oxidations by the Reagent ‘H_2O_2−Vanadium Derivative−Pyrazine-2-carboxylic Acid’”. For parts 1−15, see refs. 10a−o, respectively. Preliminary communications,[11] reviews[12] and relevant papers[13] have been also published.

* Author to whom correspondence should be addressed. Phone: +(7495)-9397317. Fax: +(7495)1376130 or +(7495)9397417. E-mail: shulpin@chph.ras.ru or gbsh@mail.ru.

[‡] Semenov Institute of Chemical Physics.

[§] Université de Neuchâtel.

[⊥] Clemson University.

[||] University of Debrecen.

10.1021/jp0700884 CCC: $37.00

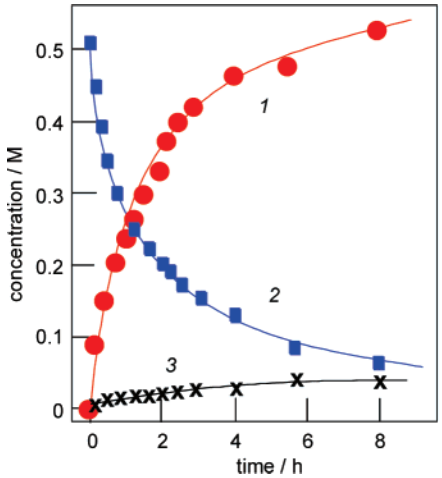


Figure 1. Oxidation of isopropanol (12.4 M) with H_2O_2 ($[H_2O_2]_0$ = 0.51 M) in the presence of water (2.2 M) catalyzed by n-Bu_4NVO_3 (1 mM) and PCA (4 mM) at 50 °C in air. Accumulation of acetone (curve 1), consumption of hydrogen peroxide (curve 2), and consumption of O_2 from air (curve 3) with time are shown.

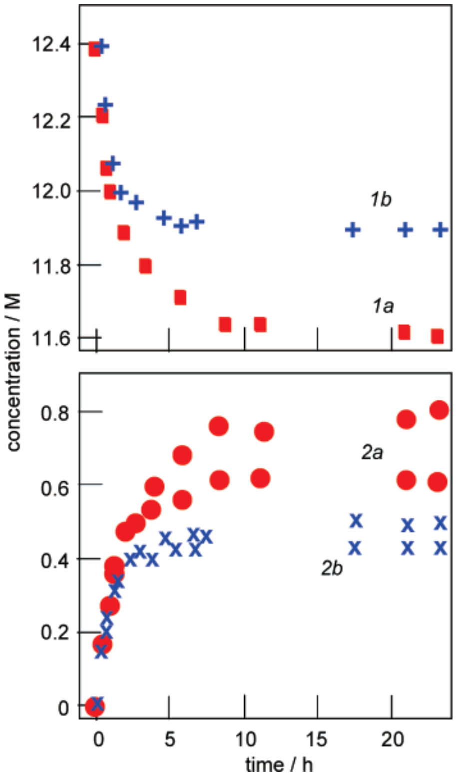


Figure 2. Oxidation of isopropanol (12.4 M) with H_2O_2 (0.5 M) in the presence of water (2.2 M) catalyzed by n-Bu_4NVO_3 (1 mM) and PCA (4 mM) at 50 °C in air (points a) and in an argon atmosphere (points b). Consumption of isopropanol (points 1) and accumulation of acetone (points 2) with time are shown. Data for accumulation of acetone were taken from two independent experiments.

In the present work, we have studied the 2-propanol oxidation with the vanadate−PCA reagent to obtain further understanding of the mechanism of the reagent action. It was also important to compare the mechanisms of oxidation of alkanes and alcohols.

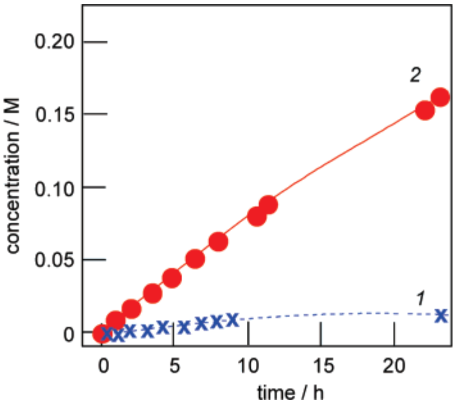


Figure 3. Accumulation of acetone in oxidation of isopropanol (12.4 M) with air in the presence of low concentration of H_2O_2 ($[H_2O_2]_0$ = 0.01 M) and water (2.2 M) catalyzed by n-Bu_4NVO_3 (1 mM) in the absence (curve 1) and in the presence of PCA (4 mM; curve 2) at 50 °C in air.

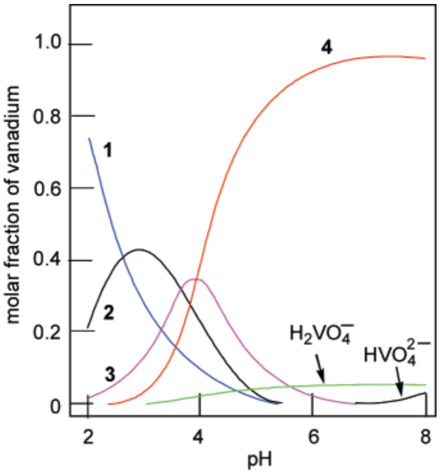


Figure 4. Concentration distribution curves for the vanadium(V)/PCA system ($c_{V(V)}$ = 1.0 mM at a metal to ligand ratio of 1:4).

TABLE 1: Composition and Stability Constants of Proton (log K) and Vanadium(V) (log β) Complexes of PCA = pcaH at 25.0 °C and I = 0.20 M (KCl)

species	M	pca	H	log K/log β
pcaH	0	1	1	2.696(5)
$[VO_2(pca)(H_2O)_2]$	1	1	3	19.77(4)
$[VO_2(pca)_2]^-$	1	2	3	22.53(8)
$[VO_2(pca)(H_2O)(OH)]^-$	1	1	2	15.96(9)
$[VO_2(pca)(OH)_2]^{2-}$	1	1	1	11.40(8)

[a] Standard deviations are in parentheses.

2. Experimental Section

The catalytic oxidation reactions were carried out usually in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was usually 10 mL, and the temperature was 40 or 50 °C. Initially, a portion of H_2O_2 (30% aqueous, Fluka, nonstabilized) was added to the solution of the catalyst, cocatalyst, and substrate. After certain time intervals samples (0.6 mL) were taken. To determine concentrations of 2-propanol, acetone and cyclohexane oxidation products the samples of reaction solutions were analyzed after their treatment with solid PPh_3 (generally, this method allows us to estimate concentration of the alkyl hydroperoxide formed in oxidation of the alkane; see refs 10g, 12c,d, and 17) by gas chromatography (instrument “DANI-86.10”; fused silica capillary columns 25 m × 0.32 mm × 0.25 μm and stationary phase CP-WAX52CB; integrator SP-4400; carrier gas helium). For the reagents used and for other details, see our previous papers on the oxidations by the same reagent.[10,11]

For the pH−potentiometric measurements the vanadium(V) solution was made by dissolving $NaVO_3$ (BDH) in diluted KOH solution of known concentration. The metal ion concentration

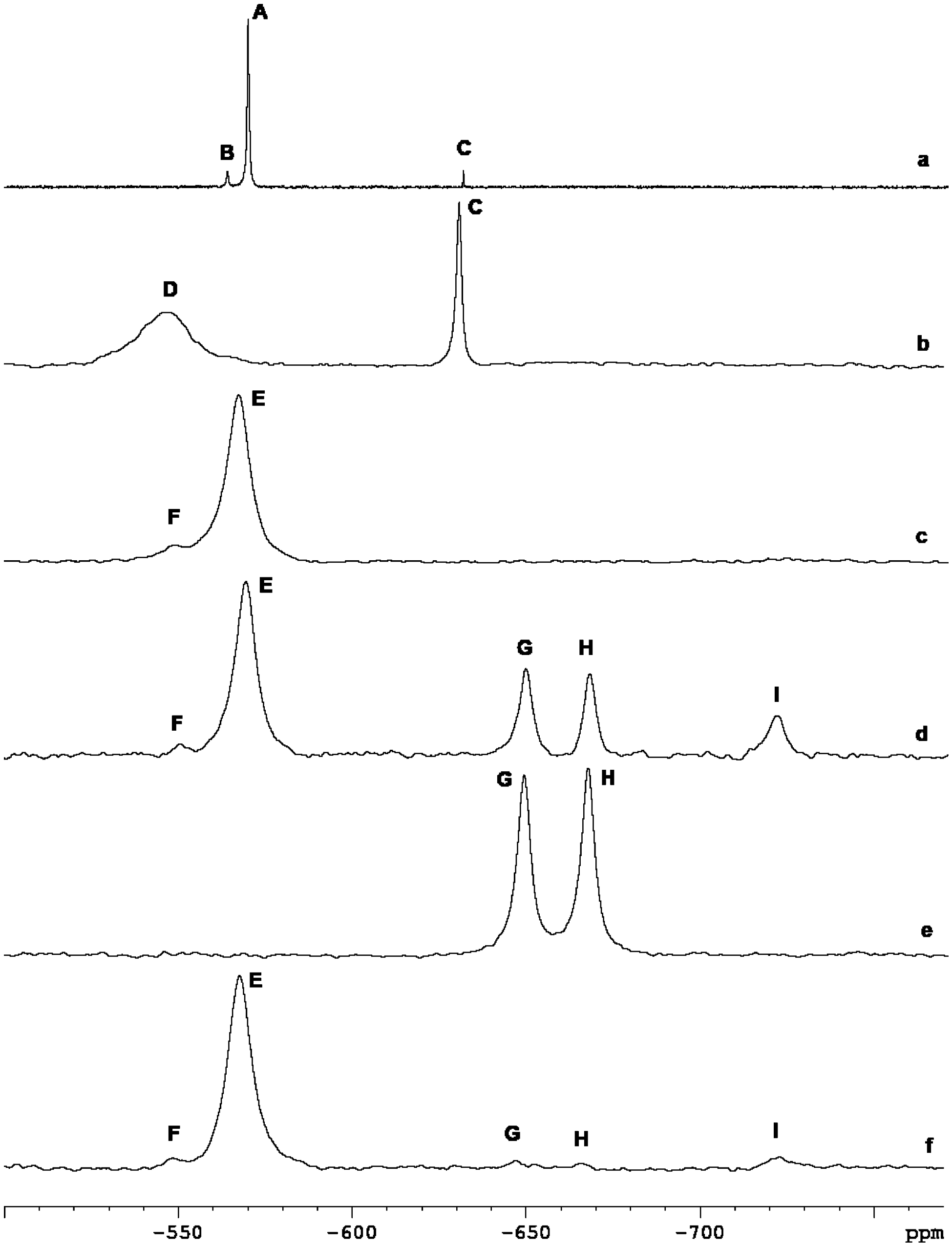


Figure 5. ^{51}V NMR spectra of (a) *n*-Bu_4NVO_3 (1 mM); (b) *n*-Bu_4NVO_3 (1 mM) + PCA (4 mM); (c) *n*-Bu_4NVO_3 (1 mM) + PCA (4 mM) + H_2O_2 (1 mM); (d) *n*-Bu_4NVO_3 (1 mM) + PCA (4 mM) + H_2O_2 (0.5 M); (e) *n*-Bu_4NVO_3 (1 mM) + H_2O_2 (0.5 M); (f) *n*-Bu_4NVO_3 (1 mM) + PCA (12 mM) + H_2O_2 (0.5 M). All spectra were recorded in isopropanol containing 2.2 M H_2O.

was determined gravimetrically by precipitation of the quinolin-8-olate. The exact concentrations of the ligand stock solutions were determined by the Gran's method.[16a] pH−potentiometric measurements were carried out at an ionic strength of 0.2 M (KCl) and at 25.0 ± 0.1 °C in aqueous solution. Carbonate-free KOH solution of known concentration (ca. 0.2 M) was used as a titrant. A Radiometer pHM 84 instrument equipped with a Metrohm combined electrode (type 6.0234.110) and a Metrohm 715 Dosimat burette was used for the pH-metric measurements. The electrode system was calibrated according to Irving et al.;[16b] the pH-metric readings could therefore be converted directly into hydrogen ion concentration. The water ionization constant, pK_w, is 13.76 ± 0.01 under the conditions employed. The pH-metric titrations were performed in the pH range of 2.0−11.0. The initial volume of the samples was 10.00 mL. The ligand concentrations were varied in the range of 2−4 mM, and the metal ion to ligand ratios in the range 1:1−1:4. The samples were in all cases completely deoxygenated by bubbling purified argon for ca. 20 min before the measurements. About 200 titration points were used to find the stoichiometry of the species and calculate their concentration stability constants in the V(V)−PCA system. The calculations were performed by the PSEQUAD computer program[16c] using the literature data (log β) of the vanadium(V)[16d] hydrolytic species. (The Davies equation was used to take into account the different ionic strengths; H_{-1} relates to the metal-induced ionization of the coordinated water). The accepted fitting of the titration curves was always less than 0.01 cm^3.

NMR spectra were recorded on a Bruker Avance 500 at 500.13 MHz (^{1}H) and 131.46 MHz (^{51}V). A typical vanadium spectrum for a 1 mM solution was obtained from the accumulation of 20 000 transients with a 700 ppm spectral window at about 12 scans per second. Unless it is stated otherwise, spectra were recorded at room temperature (297 K). An exponential line broadening up to 200 Hz was applied before Fourier transformation. The vanadium chemical shifts are quoted relative to external $VOCl_3$ (0 ppm). The spectra in 2-propanol were collected with the magnetic field unlocked. To allow direct comparison with the kinetic catalytic data, for all isopropanol samples the concentration of water was maintained at the same level of 2.2 M. Electronic spectra were taken using a Uvicon-930 spectrophotometer in quartz cuvettes (1 cm).

3. Results and Discussion

3.1. Main Features of the Oxidation of 2-Propanol. We found that isopropanol can be easily oxidized to acetone by hydrogen peroxide in air when the vanadate anion in the form of its tetrabutylammonium salt, *n*-Bu_4NVO_3, is used as a catalyst and PCA as a cocatalyst (Figure 1). A small amount of molecular oxygen is simultaneously evolved. PCA added to the reaction solution dramatically accelerates the transformation of 2-propanol to acetone (see below, Figure 16).

The yield of acetone is lower, if the reaction is carried out in an argon atmosphere (Figure 2). This suggests that atmospheric oxygen takes part in the oxidation, although the initial rates of the reaction in argon and in air are the same. In our kinetic study described below we measured only initial rates of the oxidation.

Isopropanol is slowly oxidized with atmospheric oxygen. This reaction is also catalyzed by vanadate, but only in the presence of a small concentration of hydrogen peroxide (see refs 8a,b). It is interesting that in this case PCA also accelerates the reaction (Figure 3).

To obtain a mechanistic understanding of this oxidation process, first of all we studied the composition of the reaction mixture by titration as well as spectroscopic and kinetic methods described in the following sections.

3.2. Speciation in the H^+/VO_3^-/PCA System. The distribution of various vanadium complexes in solution was studied in ref 18. We investigated for the first time the distribution of various species in the system consisting of a vanadate ion and PCA at different pH values. PCA exhibits one proton dissociation process in the measurable pH range. The dissociation constant determined as shown in Table 1 is in excellent agreement with values determined earlier under slightly different experimental conditions (2.76 ($I = 1.0$ M); 2.7 ($I = 0.5$ M)).[19a,b] The deprotonation of PCA takes place obviously at N(1). The basicity of the carboxylate group is very weak due to the formation of an internal hydrogen bond between the carboxylate group and N(1)H; thus it may only protonate in strongly acidic medium.

Equilibrium D defining the overall reactions between the vanadium-containing ion and PCA as well as the overall stability constants of the complexes formed can be defined as follows

$$HVO_4^{2-} + q\text{pca}^- + rH^+ \rightleftharpoons [VO_2\text{pca}_qH_{r-3}]^{r-2-q} + 2H_2O \qquad \text{(D)}$$

$$\beta = \frac{[VO_2\text{pca}_qH_{r-3}]^{r-2-q}}{[HVO_4^{2-}][\text{pca}^-]^q[H^+]^r}$$

For V(V) where numerous species are copresent but the free metal ion does not exist in aqueous solution, as usual, HVO_4^{2-} is chosen as component M in the calculations. The stoichiometry and stability constants of the complexes yielding the best fit of the experimental titration curves are summarized in Table 1, while the speciation curves calculated for the 1:4 metal ion to ligand ratio are depicted in Figure 4. As it is shown, the metal−ligand system is well-described by 1:1 species with different protonation degrees, and the fit is improved significantly with the additional assumption of $[VO_2(\text{pca})_2]^-$. At acidic pH the complexation starts with the species $[VO_2(\text{pca})(H_2O)_2]$, in which the ligand coordinates via N,O-chelate (species **1**). Upon increasing the pH, formation of $[VO_2(\text{pca})_2]^-$ (species **2**) and, parallel to it, deprotonation of one of the water molecules coordinated to the metal ion may take place yielding $[VO_2(\text{pca})(H_2O)(OH)]^-$ (species **3**). Above pH 4.5 a further base consumption process occurs that can be fitted best with the assumption of the formation of $[VO_2(\text{pca})(OH)_2]^{2-}$ (species **4**). Above pH 5, monovanadate is also present, especially when the PCA excess is smaller.

Direct comparison of the stability constants (Table 1) with the results for the V(V)−pic system (pic = pyridine-2-carboxylate; PIC = picolinic acid) obtained by combined potentiometric and ^{51}V NMR techniques[18b] is not possible because of the different definition of vanadium as a component ($H_2VO_4^-$ vs HVO_4^{2-}) and the different basicity of the ligands (5.170 vs 2.696). For comparison of the stability of the chelate(s) with the two ligands, therefore, the equilibrium constants (K_i*) for the following proton displacement reactions were calculated

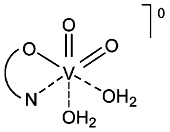
$$H^+ + H_2VO_4^- + \text{pcaH} \rightleftharpoons [VO_2(\text{pca})(H_2O)_2]$$

where K_1* refers to the formation of one N,O-chelate, or

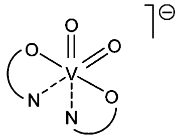
$$H_2VO_4^- + 2\text{pcaH} \rightleftharpoons [VO_2(\text{pca})_2]^- + 2H_2O$$

where K_2* refers to the formation of two N,O-chelates.

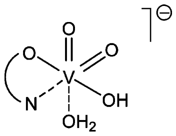
Using data taken from ref 18b and Table 1 the calculated log K_1* (PIC, 8.89; PCA, 8.90) or log K_2* (PIC, 8.58; PCA, 8.96) values indicate very similar binding strengths of these ligands and also prove the coordination mode (i.e., the formation of N,O-chelate(s)) for the PCA complexes.



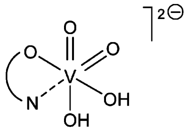
1



2



3



4

3.3. NMR Spectra. A vanadium spectrum of a 1 mM solution of Bu_4NVO_3 in isopropanol is shown in Figure 5a. All signals observed in this spectrum have line widths ($W_{1/2}$) below 100 Hz, and in this case we applied a relatively small line broadening when processing the free induction decay (5 Hz). The spectrum consists of a major peak at −570 ppm ($W_{1/2} = 80$ Hz) (A) and two minor peaks at −563 ppm ($W_{1/2} = 80$ Hz) (B) and −631 ppm ($W_{1/2} = 26$ Hz) (C). Two signals in the low field are located in a region typical for vanadate alkyl esters in isopropanol,[8a] while peak B is considerably shifted upfield from that region. Analysis of the literature data shows that the compound VO(O-*i*-Pr)$_3$ gives rise to a very sharp vanadium signal around −630 ppm.[20] Therefore, on the basis of the chemical shift and the line width, resonance C can be ascribed to VO(O-*i*-Pr)$_3$, which forms from Bu_4NVO_3 in *i*-PrOH at minor quantities (3% of overall vanadium concentration). Addition of trifluoroacetic acid in excess to this solution leads to complete conversion of

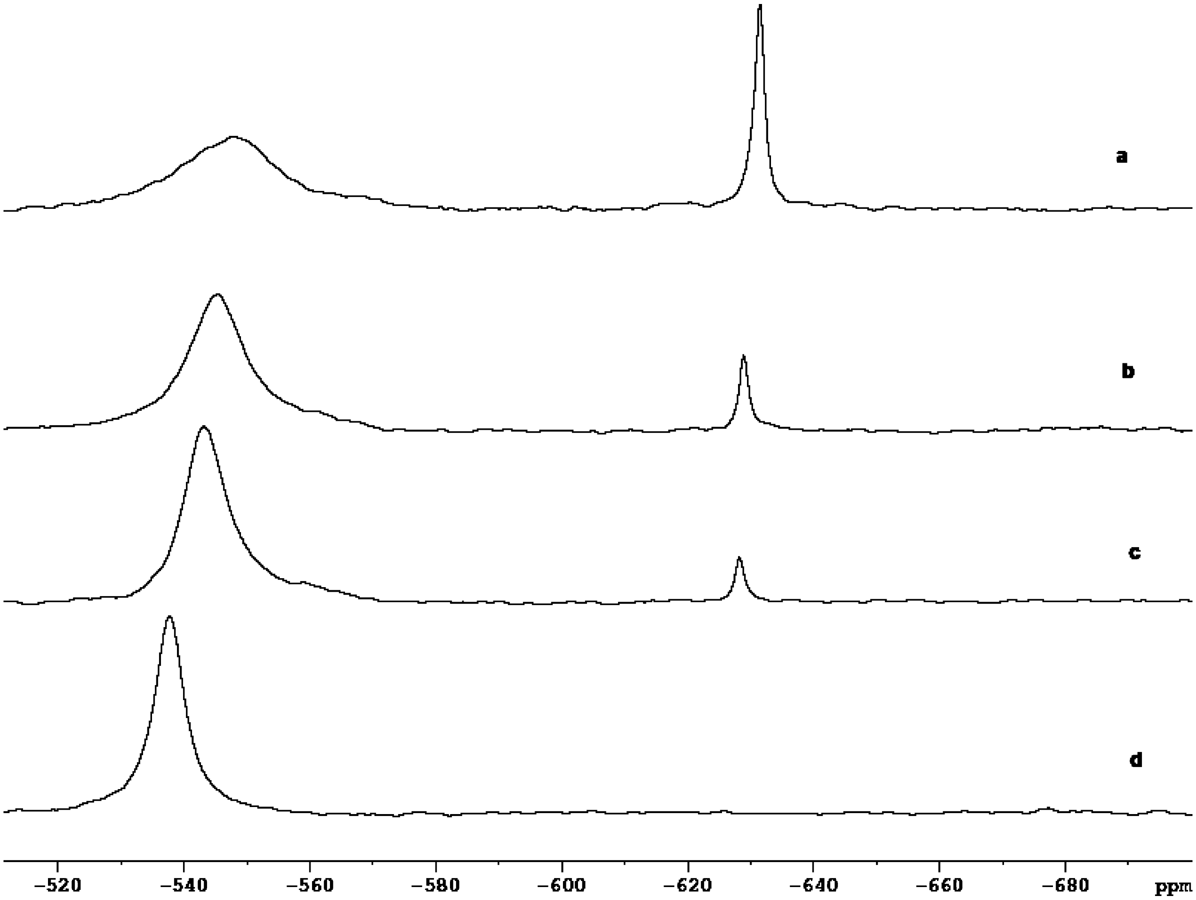


Figure 6. ^{51}V NMR spectra of n-Bu$_4$NVO$_3$ (1 mM) + PCA (4 mM) in acetonitrile/isopropanol volume mixtures (CD$_3$CN/i-PrOH = χ): (a) $\chi = 0$; (b) $\chi = 0.25$; (c) $\chi = 0.50$; (d) $\chi = 1.00$. All solutions contained 2.2 M H$_2$O.

all other species in VO(O-i-Pr)$_3$, and the ^{51}V NMR spectrum consists of a single signal at −631 ppm (Figure S1 of the Supporting Information).

In the presence of 4-fold excess of PCA, the spectrum of Bu$_4$NVO$_3$ in isopropanol consists of two signals (Figure 5b). The high-field signal is the same as resonance C in the first spectrum, arising from VO(O-i-Pr)$_3$. The relative intensity of this signal significantly increases in the presence of PCA (from 3% to 28% of overall vanadium concentration). Clearly PCA also facilitates the formation of VO(O-i-Pr)$_3$ from Bu$_4$NVO$_3$ in i-PrOH. A second signal observed in spectrum 2b at −546 ppm (D) is very broad ($W_{1/2}$ = 2500 Hz), and it originates from a vanadium complex with PCA. To identify this complex, we can use the results obtained for acetonitrile as a solvent. The system n-Bu$_4$NVO$_3$−PCA in acetonitrile-d_3 was studied by ^{51}V and ^{1}H NMR earlier. It was shown that addition of PCA to n-Bu$_4$NVO$_3$ leads to the formation of anions [VO$_2$(pca)$_2$]$^-$ with no other vanadium species present at PCA:V > 2:1.[21] In acetonitrile-d_3 this complex had a vanadium chemical shift −532 ppm (−538 ppm in the presence of 2.2 M H$_2$O), which is close to the chemical shift of D observed in isopropanol in the current work.[22]

The ^{1}H NMR spectrum of an acetonitrile solution of [VO$_2$(pca)$_2$]$^-$ in the aromatic region consists of three signals at 9.22, 8.77, and 8.45 ppm, as expected considering its symmetry. (Each pca ligand has three nonequivalent aromatic protons, the two pca ligands being equivalent.[10l]) The proton spectrum of 1 mM V + 4 mM PCA in isopropanol shows three signals from free PCA (9.25, 8.81, and 8.77 ppm) and three signals of equal intensity from a V−PCA complex with chemical shifts relatively close to those observed in CD$_3$CN (9.30, 8.96, and 8.65 ppm) (Figures S2 and S3 of the Supporting Information). On the basis of close NMR chemical shifts, we assume that the structure of the V−PCA species is similar in both solvents. Slightly different chemical shifts of pca ligands may be due to different compositions of the solvation shell in these two solvents.

The significant difference in the ^{51}V NMR line widths (2400 Hz in isopropanol vs 450 Hz in acetonitrile) can be explained by difference in the solution viscosities. The NMR line width of vanadium-51 is controlled by quadrupolar relaxation, and it is proportional to the rotational correlation time τ_c, which in turn is proportional to the viscosity. The ratio of the line widths for D in isopropanol and for [VO$_2$(pca)$_2$]$^-$ in acetonitrile is roughly the same as the ratio of viscosities of isopropanol and acetonitrile at room temperature (2.04 and 0.34 mPa s, respectively).[23] In mixed acetonitrile−isopropanol solvents of different compositions, we observed gradual changes in vanadium NMR spectra on transition from pure acetonitrile to pure isopropanol. The signal from [VO$_2$(pca)$_2$]$^-$ broadened, and the concentration of VO(O-i-Pr)$_3$ increased with increasing relative content of isopropanol (Figure 6). The vanadium spectra obtained in binary solvents contained no new, previously undetected resonances.

Visually, the signal from VO(O-i-Pr)$_3$ (C) in Figure 5 seems broader in the presence of PCA than in the absence of it (spectra 5a and 5b). On the first glance, it could be interpreted as an indication of some structural changes generated by PCA for this complex. However, this effect is only apparent and it results from exponential multiplication with a strong line broadening (200 Hz) applied for reliable detection of very broad signal D.

When we process spectra 5a and 5b with the same line broadening, the line widths of signal C in these spectra are identical.

Addition of 1 mM of H_2O_2 to the solution results in dramatic transformations experienced by the vanadate species. Both signals C and D vanish, while a new major resonance E appears (δ −568 ppm, $W_{1/2}$ 760 Hz) (Figure 5c). Though peak E is considerably sharper than signal D, it is still much broader that the major resonance in similar mixtures in acetonitrile[10l] (760 vs 135 Hz). Once again, the ratio of the line widths in isopropanol and in acetonitrile is roughly the same as the ratio of their viscosities, while the chemical shifts are rather close. This fact may be considered as evidence of a similar structure for peroxo species formed in these two solvents.

Even stronger evidence of similarity of their structures comes from the proton data. The proton spectrum of the V/PCA/H_2O_2 mixture in the aromatic region shows six new resonances in addition to three signals from free PCA. Two of these resonances overlap giving a signal of double intensity (δ 9.92 (1 H), 9.46 (1 H), 9.40 (2 H), 9.38 (1 H), and 9.21 (1 H)) (Figure S3 of the Supporting Information). A similar pattern was observed[10l] in acetonitrile-d_3, and it was explained by the formation of the oxo−peroxo complex containing anion $[V(O)(O_2)(pca)_2]^-$. This species has a pentagonal bipyramidal structure with two nonequivalent pca ligands.[13c] All six aromatic protons in this complex are nonequivalent, which should result in six different proton signals in the aromatic region. We believe that a peroxo−vanadate complex responsible for resonance E includes the same moiety.

Obviously, this species is coordinatively saturated (vanadium is heptacoordinated), and it has no easily exchangeable ligands. It was suggested earlier that presence of such labile ligands could serve as a requisite for the reactivity of peroxo vanadium complexes.[24] If this hypothesis is correct, our NMR data do not support the model where the oxo−peroxo species E acts as catalytic centers in the presence of PCA. This complex seems stable and even can be separated and characterized.[13c] Once again, there is some difference in proton chemical shifts of pca ligands in acetonitrile and in isopropanol, which may serve as an indication of involving alcohol molecules into the outer sphere of vanadium species. These changes are too subtle, however, to consider them as strong evidence of entering isopropanol into the first coordination sphere of vanadium for these oxo−peroxo complexes.

Spectrum 5c contains also a minor component F at −547 ppm, which is at about the same position as absorption D in spectrum 5b (Figure 5). We think, however, that these resonances belong to different species. First, absorption **D** seems to be considerably broader than F. (The exact line width of F was not determined because of the very low intensity of this peak.) Second, resonance F shows up with approximately the same intensity even at much higher peroxide concentrations (see Figure 5d). It is highly improbable that we have a situation where the vast majority of species D easily react with H_2O_2, while a minor amount of the same species is "peroxide-adamant". Two vanadium signals observed in the presence of peroxide in acetonitrile were tentatively assigned[10l] to two different isomers of monoperoxo anions $[V(O)(O_2)(pca)_2]^-$. Possibly peak F also belongs to a minor isomer of this complex.

Further addition of H_2O_2 produces three new vanadium resonances of comparable intensities in the high field region: δ −649 ($W_{1/2} = 400$ Hz) (G), δ −667 ($W_{1/2} = 390$ Hz) (H), and δ −721 ($W_{1/2} = 700$ Hz) (I) (Figure 5d). At 0.5 M H_2O_2 about 40−45% of all vanadium has been transformed into these new species. Interestingly, increasing peroxide concentration in acetonitrile-d_3 did not generate any new species,[10l] and this fact may explain the very different properties of these two solvents when we deal with the reactivity of the "V−PCA−H_2O_2" reagent.

To identify the new complexes, we recorded the spectrum obtained under the same conditions as in Figure 5d but with one exception: no PCA was added. It turned out that the two low-field signals (G and H) form also without PCA. Furthermore, they are the only signals observed in such mixtures (Figure 5e). Conte and co-workers[8a] studied n-Bu_4NVO_3 in different nonaqueous solvents in the presence of H_2O_2 and in isopropanol observed the spectrum containing two signals at about the same positions. The upfield component was attributed to aqua-diperoxovanadium species, while the downfield resonance to diperoxo species containing alcohol. We believe that the same complexes are responsible for signals G and H in our vanadium spectra. Similar intensities of signals G and H in spectra 5d and 5e are of accidental nature resulting from close concentrations of these diperoxo complexes at the water concentration that we used (2.2 M). At higher water concentrations the relative intensity of aqua species H grows and exceeds the intensity of alcohol-containing species G.

The ^{51}V NMR signal of species I is located in the range typical for diperoxo vanadate complexes,[25] and we can safely assume that this species also contains two peroxo ligands. The exact composition of other ligands present in the metal coordination sphere of I is still unknown. We know, however, that no diperoxo species were observed in acetonitrile under similar conditions.[10l] Besides, as we discussed earlier, species I is not formed in the absence of PCA. On the basis of these two facts, we assume that the coordination sphere of diperoxovanadate I can include both PCA and O-i-Pr ligands.[26]

The monoperoxo−diperoxo conversion is less efficient at higher PCA concentrations (Figure 5f). It is reasonable to assume that PCA competes with H_2O_2 for coordination sites and, at high concentrations, stabilizes monoperoxo complexes $[V(O)(O_2)(pca)_2]^-$, thus suppressing the formation of the diperoxo species. Obviously, there should be some "optimal" PCA concentration at which the degree of such monoperoxo−diperoxo conversion reaches the maximum.

3.4. Electronic Spectra. A study of the NMR spectra of the vanadate anion in the presence of hydrogen peroxide and PCA in isopropanol (see section 3.3) demonstrated that in the system both mono- and diperoxo vanadium complexes are formed. These complexes can contain pca anions in the vanadium coordination sphere. The data obtained by the UV−vis investigation also support the formation of peroxovanadium complexes containing pca ligands. We found that addition of PCA to the vanadate (10^{-3} M) and H_2O_2 (0.5 M) solution in 2-propanol containing water (2.2 M) leads to the appearance of a new absorption band in the visible region with a maximum at 457 nm (Figure 7). As this absorption is not observed in the absence of either H_2O_2 or PCA, we have to attribute this band to the formation of a peroxovanadium complex containing the PCA molecule in the coordination sphere. The intensity of absorption D_{457} increases with growth of concentration of added PCA, attains maximum value at $[PCA] > 10^{-2}$ M, and remains constant upon subsequent increase of the PCA concentration (Figure 8, curve 2). The maximum value of optical absorption in this case is close to the value that was obtained for the higher H_2O_2 concentration (0.5 M, compare Figure 8, curve 1); however, this maximum is attained at a lower initial concentration of added PCA ($[PCA]_0 > 6 \times 10^{-3}$ M). Thus, the maximum

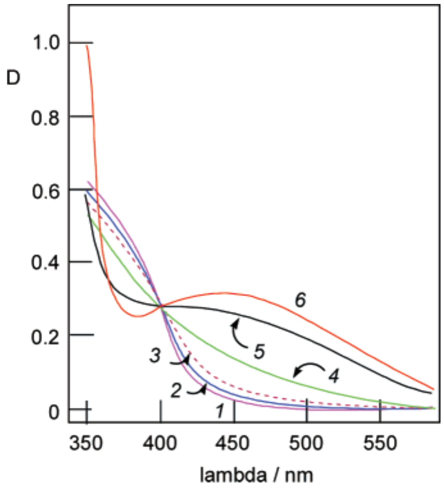


Figure 7. Electronic spectra of the solution of *n*-Bu_4NVO_3 (1 mM) and H_2O_2 (0.5 M) in isopropanol containing water (2.2 M) at various concentrations of added PCA: 0.0 (1), 0.001 (2), 0.0015 (3), 0.003 (4), 0.006 (5), 0.015 (6) M. Components were mixed in a cuvette, and after 2 min the spectra were taken (50 °C).

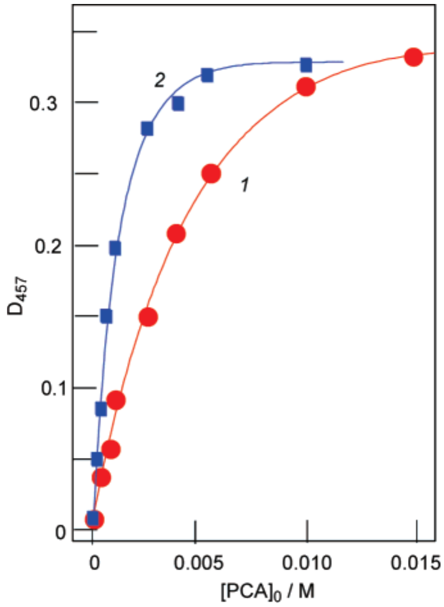


Figure 8. Dependence of the D_{457} value on the concentration of PCA added to the solution of *n*-Bu_4NVO_3 (1 mM), water (2.2 M), and H_2O_2 at two different concentrations (0.5 M: curve 1 and 0.004 M: curve 2) in 2-propanol at 50 °C.

value of optical absorption at 457 nm practically depends on neither H_2O_2 concentration (in the 0.004−0.5 M region) nor on PCA concentration (in the 0.01−0.024 M region).

The value of maximum optical absorption D_{457} is directly proportional to the concentration of vanadate at constant concentrations of all other components (Figure S5 of the Supporting Information). This is in accordance with an assumption that under the experimental conditions practically all vanadate exists in the solution in the form of a peroxo complex containing PCA in the coordination sphere. Figure 9 demonstrates changes in absorption spectra of the solution of vanadate (10^{-3} M) and PCA (10^{-2} M) upon addition of various concentrations of hydrogen peroxide at a constant concentration of water (2.2 M). It follows from these data that at low H_2O_2 concentrations ($\leq$0.004 M) the optical absorption with a maximum at 457 nm increases, which corresponds to the growth of concentration of a peroxovanadium complex containing PCA in the coordination sphere (Figure 10a). However, at a 4-fold excess of H_2O_2 concentration over the concentration of the vanadate, it is possible to detect the almost complete transformation of a V−PCA complex into its peroxo derivative. The linear dependence of the increase in the D_{457} absorption on concentration of hydrogen peroxide in the initial region ($[H_2O_2]_0 = 0-0.004$ M) allows us to propose that absorption at D_{457} is due to a monoperoxo derivative. At higher concentrations of added hydrogen peroxide (0.02−0.5 M) there is some decrease of the monoperoxo complex concentration that can correspond to its transformation to a diperoxo derivative with its absorption maximum in the short-wave region of the spectrum (Figure 9b). Similar effects become even more obvious in the spectrum obtained at a lower (0.004 M) concentration of PCA (Figure S6 of the Supporting Information).

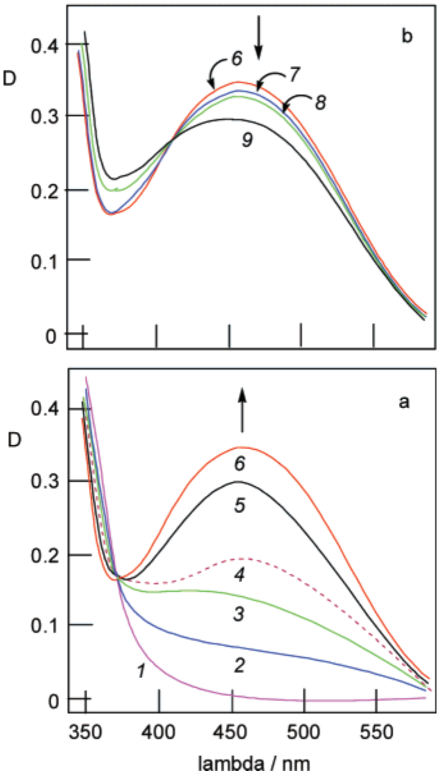


Figure 9. Electronic spectra of the solution of *n*-Bu_4NVO_3 (1 mM) and PCA (0.01 M) in isopropanol containing water (2.2 M) at various concentrations of added H_2O_2: 0.0 (1), 0.0002 (2), 0.0004 (3), 0.0006 (4), 0.001 (5), 0.004 (6), 0.024 (7), 0.025 (8), 0.50 (9) M. Components were mixed in a cuvette and after 2 min the spectra were taken (50 °C).

Changes of absorption at D_{457} (which reflects the concentration of a monoperoxo complex with PCA) upon increase of $[H_2O_2]_0$ at various concentrations of PCA are shown in Figure 10b. It can be concluded that the lower concentration of PCA the lower H_2O_2 concentration is required to attain the maximum concentration of the monoperoxo complex (compare curves 1, 2, and 3 in Figure 10a). Simultaneously, if the concentration of PCA is low, then the transformation of monoperoxo to diperoxo derivatives occurs to high extent even when hydrogen peroxide is added in a small amount (compare Figure 10, curves 1, 2, and 3). These results testify that PCA and H_2O_2 compete for a site in the coordination sphere of vanadium.

On the basis of the above-described NMR and UV−vis spectroscopic data we propose the following scheme for the description of equilibrium transformations in the vanadate−H_2O_2−PCA system in 2-propanol containing water

$$\text{“V”} + \text{PCA} \rightleftharpoons \text{“V(PCA)”} \quad K_1 \qquad (1)$$

$$\text{“V(PCA)”} + \text{PCA} \rightleftharpoons \text{“V(PCA)}_2\text{”} \quad K_2 \tag{2}$$

$$\text{“V”} + \text{H}_2\text{O}_2 \rightleftharpoons \text{“V(H}_2\text{O}_2\text{)”} \quad K_3 \tag{3}$$

$$\text{“V(H}_2\text{O}_2\text{)”} + \text{H}_2\text{O}_2 \rightleftharpoons \text{“V(H}_2\text{O}_2\text{)}_2\text{”} \quad K_4 \tag{4}$$

$$\text{“V(H}_2\text{O}_2\text{)}_2\text{”} + \text{PCA} \rightleftharpoons \text{“V(H}_2\text{O}_2\text{)}_2\text{(PCA)”} \quad K_5 \tag{5}$$

$$\text{“V(H}_2\text{O}_2\text{)}_2\text{(PCA)”} \rightleftharpoons \text{“V(H}_2\text{O}_2\text{)(PCA)”} + \text{H}_2\text{O}_2 \quad K_6 \tag{6}$$

$$\text{“V(H}_2\text{O}_2\text{)(PCA)”} + \text{PCA} \rightleftharpoons \text{“V(H}_2\text{O}_2\text{)(PCA)}_2\text{”} \quad K_7 \tag{7}$$

In these equations V is a schematic symbol for the vanadate anion, and we formally consider both PCA and H_2O_2 as indivisible ligands. These ligands can be conventionally added or replaced as a whole in various reactions. The first two equations purposely simplify the situation since the real stoichiometry of the stages should be written by reactions 1a and 2a

$$\text{VO}_3^- + \text{pcaH} + 2\text{H}_2\text{O} \rightleftharpoons [\text{VO}_2(\text{pca})(\text{H}_2\text{O})_2] + \text{HO}^- \tag{1a}$$

$$[\text{VO}_2(\text{pca})(\text{H}_2\text{O})_2] + \text{pcaH} + \text{HO}^- \rightleftharpoons [\text{VO}_2(\text{pca})_2]^- + 3\text{H}_2\text{O} \tag{2a}$$

In accordance with reaction 1a, the interaction of vanadate with PCA gives rise to the formation of HO^-, which will be further involved into reaction 2a, when the second PCA molecule enters the vanadium coordination sphere. Water present in substantial concentrations slightly retards the 2-propanol oxidation (see below). However, the amount of water liberated in reaction 2a should not exceed 10^{-3} M (at a standard concentration of the vanadium derivative that we used almost in all experiments). Taking into account all of these arguments, in our kinetic calculations we can replace reactions 1a and 2a by more simple reactions 1 and 2, respectively.

Reactions 1−7 do not take into account the possibility of water and/or 2-propanol entering the coordination sphere of vanadium. Concentrations of 2-propanol and water are much higher than the concentrations of all other reactants and therefore can be considered constant under the experimental conditions. In addition, in this scheme we did not consider the possibility of the formation of dimer vanadium species because we were unable to detect these species by NMR and optical absorption under all studied conditions was proportional to vanadate concentration.

An analysis of reactions 1−7 requires in the general case taking into consideration three equations of the material balance based on concentrations of the vanadate, hydrogen peroxide, and PCA, and this leads to a complicated system of equations and, as a result, to a very difficult analysis of the correspondence between the scheme and the experimental data. Such an analysis does not seem to be reasonable, taking into account a relatively low accuracy of the experimental parameters. However, the situation can be significantly simplified, if we take into account the results of experiments carried out at high concentrations of hydrogen peroxide ($[H_2O_2]_0/[V]_0 \geq 10$) and PCA ($[PCA]_0/[V]_0 \geq 10$). In this case we can consider the equilibrium concentrations of these compounds ($[H_2O_2]$ and [PCA]) to be equal to their initial concentrations (i.e., introduced into the solution concentrations $[H_2O_2]_0$ and $[PCA]_0$). Under these conditions we need to take into consideration only the equation of material balance based on the concentration of the vanadate anion.

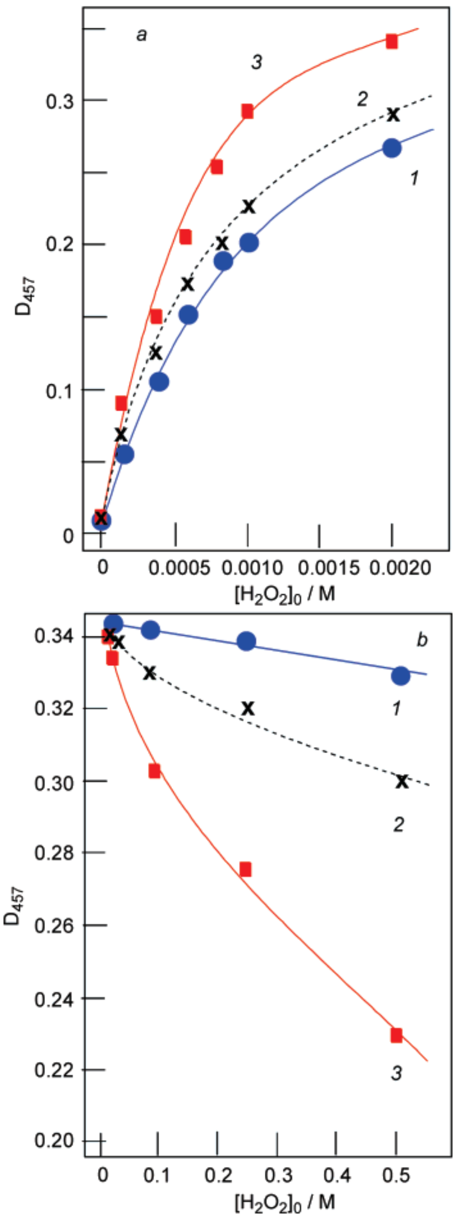


Figure 10. Dependence of D_{457} on concentration of added hydrogen peroxide in electronic spectra of the solution of n-Bu_4NVO_3 (1 mM) in isopropanol containing water (2.2 M) at three different concentrations of added PCA: 0.024 (curves 1), 0.010 (2), 0.0004 (3) M. Components were mixed in a cuvette, and after 2 min the spectra were taken (50 °C).

The data given in Figure 9b show that the diperoxo complex does not absorb at 457 nm and the maximum of this absorption is shifted to the more short-wave region. Due to this we can assume that only monoperoxo complexes “$V(H_2O_2)(PCA)$” and “$V(H_2O_2)(PCA)_2$” have significant absorption around 460 nm. Let us also assume that for these compounds the molar absorptivity parameters at 457 nm are ϵ_1 and ϵ_2, respectively. Using reactions 1−7 and assuming that $[H_2O_2]_0/[V]_0 \geq 10$ and $[PCA]_0/[V]_0 \geq 10$, we can obtain the following expression for the optical density D_{457} of the solution

$$D_{457} = \frac{K_3K_4K_5K_6[\text{H}_2\text{O}_2]_0[\text{PCA}]_0 \, (\epsilon_1 + \epsilon_2K_7[\text{PCA}]_0)[\text{V}]_0}{1 + K_1[\text{PCA}]_0 + K_1K_2[\text{PCA}]_0^{\,2} + K_3\{1 + K_4K_5K_6[\text{PCA}]_0(1 + K_7[\text{PCA}]_0)\}[\text{H}_2\text{O}_2]_0 + K_3K_4[\text{H}_2\text{O}_2]_0^{\,2}(1 + K_5[\text{PCA}]_0)} \tag{8}$$

Figure 10 shows that at $[H_2O_2] > 0.01$ M virtually all vanadium is present in the form of peroxo complexes containing PCA in the vanadium coordination sphere. Taking this into account we can simplify eq 8 for the description of dependences depicted in Figure 10b and write it as follows

$$D_{457} = \frac{K_6(\epsilon_1 + \epsilon_2 K_7[\mathrm{PCA}]_0)[\mathrm{V}]_0}{[\mathrm{H_2O_2}]_0 + K_6 + K_6K_7[\mathrm{PCA}]_0} \tag{9}$$

Curve 3 in Figure 10b does not obey the conditions discussed above because in this case $[\mathrm{PCA}]_0/[\mathrm{V}]_0 = 4$. In the case of curves 1 and 2 (Figure 10b) the decrease of D_{457} upon increase of H_2O_2 concentration is relatively small, and this allows us to assume that in the denominator of eq 9 the value of $[\mathrm{H_2O_2}]_0$ is small in comparison with the value $K_6 + K_6K_7[\mathrm{PCA}]_0$ and to transform eq 9 into the following one

$$D_{457} = \frac{(\epsilon_1 + \epsilon_2 K_7[\mathrm{PCA}]_0)[\mathrm{V}]_0}{1 + K_7[\mathrm{PCA}]_0} \left\{1 - \frac{[\mathrm{H_2O_2}]_0}{K_6(1 + K_7[\mathrm{PCA}]_0)}\right\} \tag{10}$$

In accordance with eq 10 the experimentally determined dependences corresponding to curves 1 and 2 (Figure 10b) are linear ones. These straight lines can be characterized by the *y*-intercept (α)

$$\alpha = \frac{(\epsilon_1 + \epsilon_2 K_7[\mathrm{PCA}]_0)[\mathrm{V}]_0}{1 + K_7[\mathrm{PCA}]_0} \tag{11}$$

and the ratio of the line slope and the *y*-intercept (β)

$$\beta = \frac{1}{K_6(1 + K_7[\mathrm{PCA}]_0)} \tag{12}$$

It follows from the data of Figure 10b that α does practically not depend on the concentration $[\mathrm{PCA}]_0$. This situation is possible in three cases:

(i) if the absorption D_{457} is due to species "$V(H_2O_2)(PCA)$" and $\alpha = \epsilon_1[\mathrm{V}]_0$;

(ii) if the absorption D_{457} is due to species "$V(H_2O_2)(PCA)_2$" and $\alpha = \epsilon_2[\mathrm{V}]_0$;

(iii) if the absorption coefficients of species "$V(H_2O_2)(PCA)$" and "$V(H_2O_2)(PCA)_2$" are equal, that is, $\epsilon_1 = \epsilon_2$ and $\alpha = \epsilon_1[\mathrm{V}]_0$.

The last assumption is doubtful. As the experimentally determined values of β are inversely proportional to the PCA concentration (indeed, for $[\mathrm{PCA}]_0 = 0.01$ and 0.024 M $\beta = 0.28$ and 0.11, respectively) we can say that in eq 12 the term $K_7[\mathrm{PCA}]_0 \gg 1$. This means that in the solution the species containing two PCA molecules "$V(H_2O_2)(PCA)_2$" is a predominant one ($\beta = 1/K_6K_7[\mathrm{PCA}]_0$). Using values α and β for curves 2 and 3 (Figure 10b) we can estimate molar absorptivity $\epsilon_2 = 320-360$ M^{-1} cm^{-1} and the term $K_6K_7 = 380-430$.

It turned out that if we use in calculations the equilibrium concentration $[\mathrm{PCA}]_{\mathrm{equil}}$ instead of $[\mathrm{PCA}]_0$, eq 9 also describes correctly the experimental data at $[\mathrm{PCA}]_0 = 0.004$ M (curve 3, Figure 10b). Indeed, in this case we were able to obtain a good linear dependence using coordinates $1/D_{457}$ versus $[\mathrm{H_2O_2}]_0/[\mathrm{PCA}]_{\mathrm{equil}}$ demonstrated in Figure 11. ($[\mathrm{PCA}]_{\mathrm{equil}}$ is the equilibrium concentration of PCA that is not bound to a complex with vanadium.) Taking into account the fact that under these conditions the species "$V(H_2O_2)(PCA)_2$" and "$V(H_2O_2)_2(PCA)$" are the predominant components of the solution, we can calculate the equilibrium concentration of free (nonbound with vanadium) PCA

$$[\mathrm{PCA}]_{\mathrm{equil}} = [\mathrm{PCA}]_0 - [\mathrm{V}]_0 - [\mathrm{V(H_2O_2)(PCA)_2}] \tag{13}$$

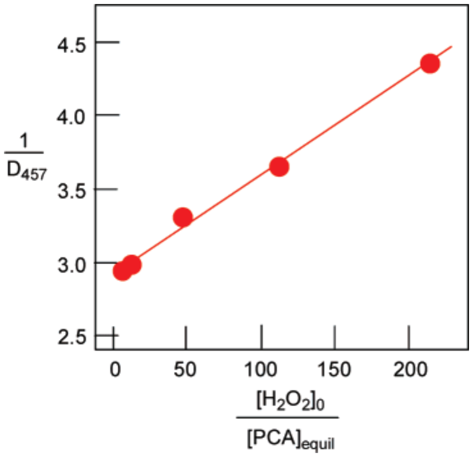


Figure 11. Dependence of parameter $1/D_{457}$ on parameter $[\mathrm{H_2O_2}]_0/[\mathrm{PCA}]_{\mathrm{equil}}$ in the electronic spectra of a solution containing *n*-Bu_4NVO_3 (1 mM) and PCA (0.004 M) in isopropanol containing water (2.2 M) at 50 °C.

From the dependence shown in Figure 11 we calculated the molar absorptivity parameter ϵ and a product of two equilibrium constants that turned out to be very close ($\epsilon_2 = 340$ M^{-1} cm^{-1}; $K_6K_7 = 430$) to the same values calculated from the data of Figure 10b (see above).

Prior to the analysis of the influence of the PCA concentration on the value of D_{457} shown in Figure 8, it is useful to note a few important points. Foremost, the NMR spectra demonstrate that in the absence of PCA practically all vanadium exists in the form of peroxo derivatives. This fact allows us to write the expression for D_{457} taking into consideration only various peroxo complexes. Second, the dependences shown in Figure 8 demonstrate that under our conditions the maximum value of absorption does not practically depend on the concentration of hydrogen peroxide. In accordance with the results described above this absorption is due to the species "$V(H_2O_2)(PCA)_2$". Consequently, when analyzing the dependence of D_{457} on $[\mathrm{PCA}]_0$ in the region that is close to the maximum absorption, we should take into consideration the absorption of species "$V(H_2O_2)(PCA)_2$" only. Using this conclusion we can write eq 8 as follows

$$D_{457} = \frac{K_5K_6K_7\epsilon_2[\mathrm{PCA}]_0^{\,2}[\mathrm{V}]_0}{K_5K_6[\mathrm{PCA}]_0(1 + K_7[\mathrm{PCA}]_0) + [\mathrm{H_2O_2}]_0(1 + K_5[\mathrm{PCA}]_0)} \tag{14}$$

Let us transform this equation into a form that is convenient for the analysis of the experimental data

$$\frac{1}{D_{457}} = \frac{1}{\epsilon_2[\mathrm{V}]_0} + \frac{K_6 + [\mathrm{H_2O_2}]_0}{\epsilon_2[\mathrm{V}]_0K_6K_7} \times \frac{1}{[\mathrm{PCA}]_0} + \frac{[\mathrm{H_2O_2}]_0}{\epsilon_2[\mathrm{V}]_0K_5K_6K_7} \times \frac{1}{[\mathrm{PCA}]_0^{\,2}} \tag{15}$$

Third, although, strictly speaking, eq 8 is correct only at $[\mathrm{PCA}]_0/[\mathrm{V}]_0 \geq 10$, we can also consider this equation at a lower concentration of PCA provided that we use the equilibrium concentration of free acid $[\mathrm{PCA}]_{\mathrm{equil}}$ instead of $[\mathrm{PCA}]_0$. The

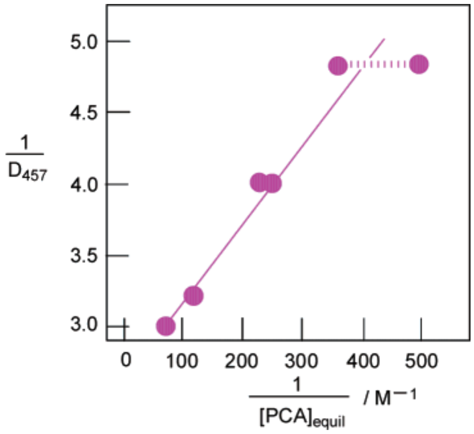


Figure 12. Dependence of parameter $1/D_{457}$ on parameter$1/[PCA]_{equil}$ in the electronic spectra of a solution containing n-Bu_4NVO_3 (1 mM), H_2O_2 (0.5 M), and water (2.2 M) in isopropanol at 50 °C.

propriety of this approach was corroborated by the results of the following analysis. We studied the dependence of D_{457} on $[H_2O_2]$ at high concentrations of hydrogen peroxide ($[H_2O_2] > 0.01$ M) where a decrease of D_{457} at $[PCA]_0 = 0.004$ M is observed. Since in the considered interval of concentrations ($[PCA]_0 = 0.004-0.015$ M) at $[H_2O_2]_0 = 0.5$ M the parameter D_{457} changes from 65% to 100% of its maximum value (Figure 8, curve 1), we can assume that in eq 15 the equilibrium concentration of PCA is located within the following interval

$$[PCA]_0 - 2[V(H_2O_2)(PCA)_2] \le [PCA]_{equil} \le [PCA]_0 - 2[V]_0 \quad (16)$$

Unfortunately, the accuracy of the experimental results is not sufficient, and a reliable preference for either linear or quadratic dependence of $1/D_{457}$ on $1/[PCA]$ is problematic. The linear dependence corresponds to the transformation of dominating species “$V(H_2O_2)(PCA)$” into “$V(H_2O_2)(PCA)_2$”, which is responsible for the absorption at 457 nm, whereas the quadratic dependence could reflect the transformation of the dominating species “$V(H_2O_2)_2$” into “$V(H_2O_2)(PCA)_2$”. The first transformation is more likely, and we used this scheme in the interpretation of the experimental dependence D_{457} on $[PCA]_0$ at $[H_2O_2]_0 = 0.5$ M (Figure 8, curve 1). The results of this analysis presented in Figure 12 allowed us to estimate the following parameters: $\epsilon_2[V]_0 = 0.4$ cm^{-1} ($\epsilon_2 = 400$ M^{-1} cm^{-1}) and $(K_6 + [H_2O_2]_0)/K_6K_7 = 2.5 \times 10^{-3}$ M. Assuming $K_6K_7 \approx 400$, we obtain $K_6 \approx 0.45$ M and, consequently, $K_7 \approx 900$ M^{-1}.

3.5. Kinetics of Oxidation of 2-Propanol to Acetone. Kinetic curves of 2-propanol oxidation are shown in Figures 1 and 2. The dependences of the initial reaction rate of acetone accumulation W_0 at various concentrations of water testify that water added to the reaction solution at a high concentration (>10 M) sufficiently retards the oxidation (Figure 13). The dependences of W_0 at various concentrations of water on initial concentrations of reactants are given in Figures 14−16. We also determined the dependence of the initial rate of 2-propanol oxidation in acetonitrile on the initial concentration of 2-propanol (Figure 17) and the dependence of the initial rates of formation of oxygenates from cyclohexane and 2-propanol on the concentration of cyclohexane in the simultaneous competitive oxidation of the alcohol and cycloalkane (Figure 18).

The kinetic data (Figures 14 and 15) demonstrate that the rate of 2-propanol oxidation is directly proportional to concentrations of the vanadate and hydrogen peroxide. An increase in the reaction rate upon growth of H_2O_2 concentration under conditions when concentrations of monoperoxo complexes with both one and two pca ligands in the vanadium sphere are constant proves that the rate-limiting step is the interaction of species “$V(H_2O_2)(PCA)_2$” (absorbing light at maximum 457 nm; see section 3.4) or species “$V(H_2O_2)(PCA)$” with a new molecule of hydrogen peroxide. This is in agreement with a proposal by Bell and co-workers that “the hydrogen transfer from coordinated hydrogen peroxide molecule to a vanadyl group... becomes the rate-determining step”.[15] Alternatively, this increase can be due to a monomolecular transformation of a diperoxo derivative, $V(H_2O_2)_2(PCA)$, concentration of which is low in comparison with concentrations of $V(H_2O_2)(PCA)_2$ and $V(H_2O_2)(PCA)$ and becomes higher at a higher H_2O_2 concentration. It should be noted that the modes of dependences of concentrations $[V(H_2O_2)(PCA)_2]$ and $[V(H_2O_2)(PCA)]$ on the H_2O_2 concentration are the same. Consequently, independence of the concentration $[V(H_2O_2)(PCA)_2]$ of the complex absorbing at 457 nm on the concentration of H_2O_2 means also that the

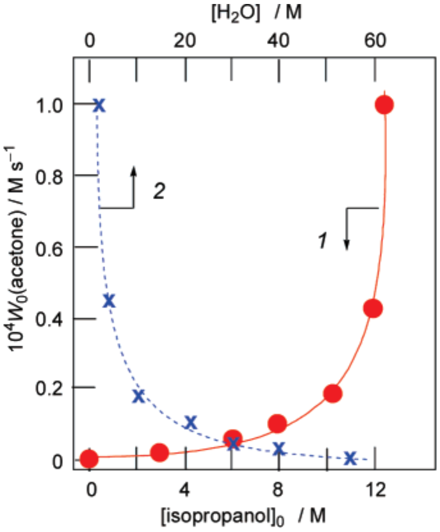


Figure 13. Dependences of the initial rate of acetone accumulation in isopropanol oxidation on the initial isopropanol concentration (curve 1) and water concentration (curve 2). Conditions: $[n\text{-}Bu_4NVO_3] = 1$ mM, [PCA] = 4 mM, $[H_2O_2]_0 = 0.50$ M, 50 °C.

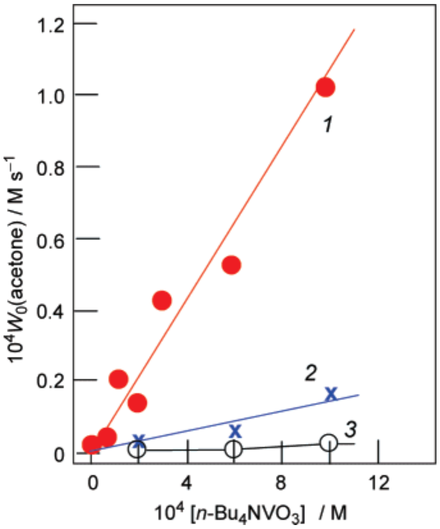


Figure 14. Dependences of the initial rate of acetone accumulation in isopropanol oxidation on the initial concentration of n-Bu_4NVO_3 at various concentrations of isopropanol and water. Curve 1: $[isopropanol]_0 = 12.4$ M; $[H_2O] = 2.2$ M. Curve 2: $[isopropanol]_0 = 10.5$ M; $[H_2O] = 10.5$ M. Curve 3: $[isopropanol]_0 = 3$ M; $[H_2O] = 42.1$ M. Conditions: [PCA] = 4 mM; $[H_2O_2]_0 = 0.50$ M; 50 °C.

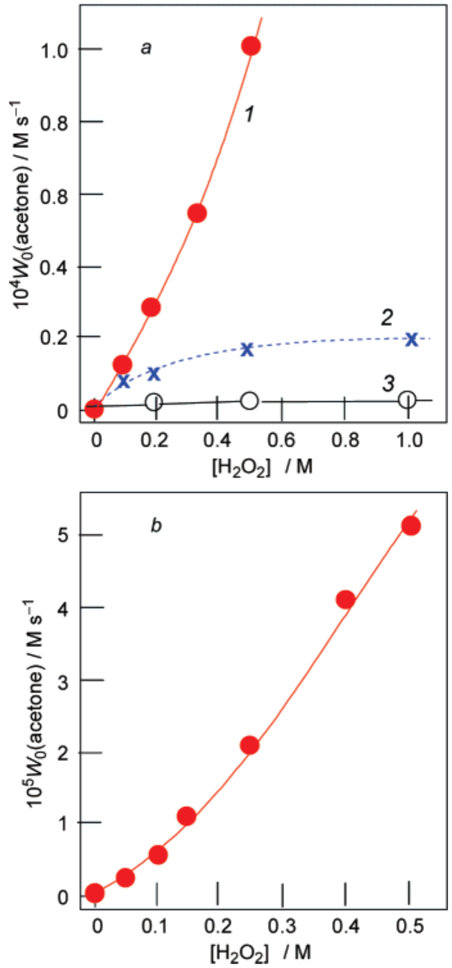


Figure 15. Dependences of the initial rate of acetone accumulation in isopropanol oxidation on the initial concentration of H_2O_2 at various concentrations of isopropanol and water. Conditions. (a) [n-Bu_4NVO_3] = 1 mM; [PCA] = 4 mM; 50 °C. Curve 1: $[\text{isopropanol}]_0 = 12.4$ M; $[H_2O] = 2.2$ M. Curve 2: $[\text{isopropanol}]_0 = 10.5$ M; $[H_2O] = 10.5$ M. Curve 3: $[\text{isopropanol}]_0 = 3$ M; $[H_2O] = 42.1$ M. (b) [n-Bu_4NVO_3] = 1 mM; [PCA] = 24 mM; $[\text{isopropanol}]_0 = 12.4$ M; $[H_2O] = 2.16-2.26$ M; 50 °C.

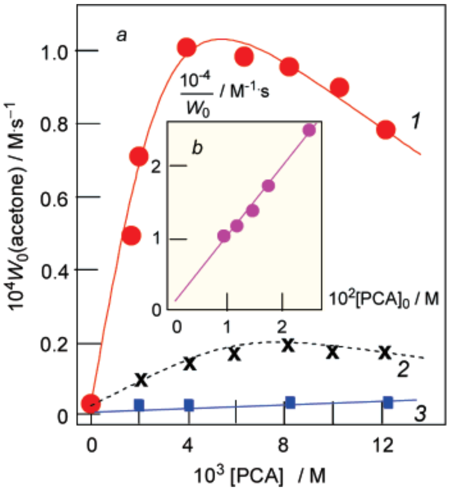


Figure 16. Dependences of the initial rate of acetone accumulation in isopropanol oxidation on the initial concentration of PCA at various concentrations of isopropanol and water. (a) Curve 1: $[\text{isopropanol}]_0 = 12.4$ M; $[H_2O] = 2.2$ M. Curve 2: $[\text{isopropanol}]_0 = 10.5$ M; $[H_2O] = 10.5$ M. Curve 3: $[\text{isopropanol}]_0 = 3$ M; $[H_2O] = 42.1$ M. (b) Dependence of the reciprocal parameter $1/W_0$ of curve 1 on the initial concentration of PCA. Conditions: [n-Bu_4NVO_3] = 1 mM; $[H_2O_2]_0 = 0.50$ M; 50 °C.

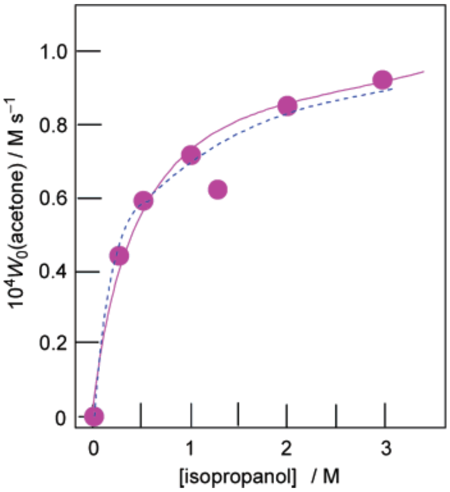


Figure 17. Dependence of the initial rate of acetone accumulation in isopropanol oxidation in acetonitrile solution on the initial concentration of isopropanol. Conditions: $[n\text{-}Bu_4NVO_3]_0 = 1$ mM; $[PCA]_0 = 4$ mM; $[H_2O_2]_0 = 0.50$ M; $[H_2O] = 2.2$ M; 50 °C.

concentration of V(H_2O_2)(PCA) is not changed upon growth of [H_2O_2]. Some decrease of the oxidation rate at $[PCA]_0 > 5 \times 10^{-3}$ M (Figure 16) is due to a decrease in concentrations of catalytically active species containing vanadium. If we accept that the rate-limiting step is the following interaction

$$\text{“V}(H_2O_2)(PCA)_2\text{”} + H_2O_2 \rightarrow ... \tag{17}$$

we can attribute a decrease of the initial rate to the equilibrium transformation

$$\text{“V}(H_2O_2)(PCA)_2\text{”} + PCA \rightleftharpoons \text{“V}(PCA)_3\text{”} + H_2O_2 \tag{18}$$

that is to a decrease of the concentration of monoperoxo complex “V(H_2O_2)$(PCA)_2$” absorbing at 457 nm. It follows from a comparison of data presented in Figure 8 (curve 1) and Figure 16 that when the oxidation rate becomes approximately 2 times lower absorption D_{457} remains practically unchanged. Consequently, reaction 17 is not a main transformation that limits the oxidation rate. Since dependences of concentrations of “V(H_2O_2)$(PCA)_2$” and “V(H_2O_2)(PCA)” on $[H_2O_2]_0$ are similar, the concentration of “V(H_2O_2)(PCA)” is practically constant when the PCA concentration increases. It means that the reaction

$$\text{“V}(H_2O_2)(PCA)\text{”} + H_2O_2 \rightarrow ... \tag{19}$$

is also not rate-limiting for the 2-propanol oxidation.

Taking into account the above consideration, we think that the most probable rate-limiting step is a monomolecular transformation of the diperoxo derivative of vanadium containing one pca ligand. This reaction can be characterized by a rate constant k.

In this case the rate retardation upon increasing [PCA] is due to the following equilibrium

$$\text{“V}(H_2O_2)_2(PCA)\text{”} + PCA \rightleftharpoons \text{“V}(H_2O_2)(PCA)_2\text{”} + H_2O_2 \tag{20}$$

which is really a sum of reactions 6 and 7 from a scheme of equilibrium transformations proposed in section 3.4. It is interesting to note that vanadium diperoxo complexes are usually more reactive in comparison with analogous monoperoxo

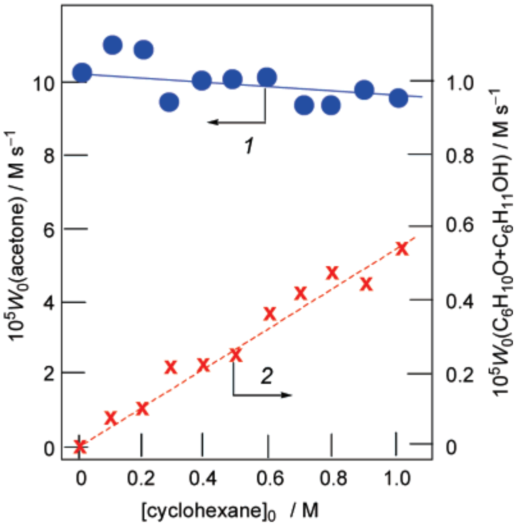


Figure 18. Dependences of the initial rates of accumulation of acetone (curve 1) and of the sum of cyclohexanone and cyclohexanol (determined after reduction with PPh_3, curve 2) in the oxidation of cyclohexane in isopropanol solution on the initial concentration of cyclohexane. Conditions: [n-Bu_4NVO_3] = 1 mM; [PCA] = 4 mM; $[H_2O_2]_0$ = 0.50 M; $[H_2O]$ = 2.2 M; 50 °C.

derivatives.[6] Thus, the oxo-diperoxovanadium complex "$OV(O_2)_2$" is much more reactive[6] toward phosphines and sulfides than the oxo-monoperoxovanadium complex "$OV(O_2)^+$" for the oxidation of the (thiolato)cobalt(III) complex, the oxo-diperoxo(picolinato)vanadium(V) complex was ca. 10^4 times more reactive that the oxoperoxo(dipicolinato)vanadium(V) complex,[27a] and triperoxodivanadium complex $(VO)_2(O_2)_3$ was the active species in the oxidation of bromide ions.[27b]

The analysis of both kinetic data and electronic spectra allows us to conclude that the main contribution to the absorption at 457 nm comes from the monoperoxo complex containing two pca ligands in the coordination sphere, namely, "$V(H_2O_2)(PCA)_2$". Assuming that the rate-limiting step of the oxidation is the transformation of the diperoxo derivative "$V(H_2O_2)_2(PCA)$", we can easily obtain the expression for the oxidation rate at $[H_2O_2]_0/[V]_0 \geq 10$ and $[PCA]_0/[V]_0 \geq 10$. Taking into account that under these conditions the vanadium exists exclusively in the form of peroxo complexes containing 0, 1, or 2 pca ligands in the coordination sphere, we come to the following equation

$$W = k[V(H_2O_2)_2(PCA)] = k\frac{K_4K_5[V]_0[H_2O_2]_0[PCA]_0}{1 + K_4K_5K_6[PCA]_0(1 + K_7[PCA]_0) + K_4[H_2O_2]_0(1 + K_5[PCA]_0)} \quad (21)$$

In the region where W_0 decreases upon growth of $[PCA]_0$, the main forms of vanadium-containing species are "$V(H_2O_2)_2(PCA)$" and "$V(H_2O_2)(PCA)_2$". Also, the electronic spectra show that the concentration of diperoxo complexes remains relatively low. On the basis of these facts we can simplify eq 21 and rewrite it as follows

$$W = k\frac{[V]_0[H_2O_2]_0}{K_6(1 + K_7[PCA]_0)} \quad (22)$$

Applying eq 22 to the experimental kinetic data, we can obtain the parameters K_6/k and K_7. According to the data shown in Figure 16b, these parameters are equal to 0.065 M s and 700 M^{-1}, respectively. Values of K_7 determined from the spectrophotometry (900 M^{-1}) and the kinetic study (700 M^{-1}) are close, which proves once again that the suggested scheme of the reaction mechanism is in a good agreement with the experimental results. Using a value of 0.45 for K_6 (see section 3.4), we can estimate the rate constant k for the monomolecular decomposition of "$V(H_2O_2)_2(PCA)$": $k \approx 7$ s^{-1}.

3.6. On the Mechanism of the 2-Propanol Oxidation: A Comparison of the Oxidation of 2-Propanol and the Oxidation of Alkanes in Acetonitrile.

To obtain an understanding of an oxidizing species generated in the catalytic system "vanadate-anion−PCA−H_2O_2" in isopropanol, we studied the competitive oxidation of three substrates, isopropanol, cyclohexane, and acetonitrile, in isopropanol and in acetonitrile. The results shown in Figure 18 testify the existence of a competition between cyclohexane and isopropanol for an active transient species (X)

$$X + Me_2CH{-}OH \rightarrow \text{products (acetone)} \quad (23)$$

$$X + CyH \rightarrow \text{products (cyclohexyl hydroperoxide)} \quad (24)$$

The rate-limiting stage of the formation of X is a monomolecular transformation of a diperoxo vanadium complex in isopropanol. If we denote the rate of the X generation as W_i, which is equal to the rate of the isopropanol oxidation (that is the rate of acetone formation) in the absence of the cyclohexane, we can write

$$W_i = \{k_{23}[Me_2CH{-}OH] + k_{24}[CyH]\}[X] \quad (25)$$

In accordance with this equation and as follows from Figure 18, the sum of the rates of formation of acetone and cyclohexyl hydroperoxide, CyOOH, remains constant at various cyclohexane concentrations. Using eq 25 we will have

$$\frac{d[CyOOH]}{dt} = k_{24}[CyH][X] = \frac{W_i}{1 + \dfrac{k_{23}[Me_2CHOH]}{k_{24}[CyH]}} \quad (26)$$

As the cyclohexane oxidation rate under all studied conditions is much lower than the isopropanol oxidation rate, we come to the following equation

$$-\frac{d[CyH]}{dt} = \frac{d[CyOOH]}{dt} = \frac{k_{24}[CyH]}{k_{23}[Me_2CHOH]} \times W_i \quad (27)$$

As follows from the data of Figure 18, the parameter W_i is equal to 10^{-4} M s^{-1}, and the slope in the linear dependence of d[CyOOH]/dt on [CyH] is equal to 5×10^{-6} s^{-1}. Taking into account that $[Me_2CH{-}OH]_0 = 12$ M, we can calculate the ratio of the rate constants in reactions 23 and 24: $k_{24}/k_{23} = 0.6$. It means that reactivities of cyclohexane and isopropanol toward species X are close.

However, the experimentally found dependence of the acetone formation rate on the concentration of isopropanol added to acetonitrile (Figure 17) shows that there is a competition between isopropanol and acetonitrile for a transient oxidizing species generated in the catalytic system in acetonitrile. This concurrence is similar to that found by us earlier in the cyclohexane oxidation in acetonitrile.[10l,11d] Selectivity parameters in the alkane oxidation by the "vanadate−H_2O_2−PCA" catalytic system in acetonitrile are low. Also, the ratios of the rates of interaction between acetonitrile or cyclohexane and a transient species formed in the "vanadate−H_2O_2−PCA" reagent (refs 10l

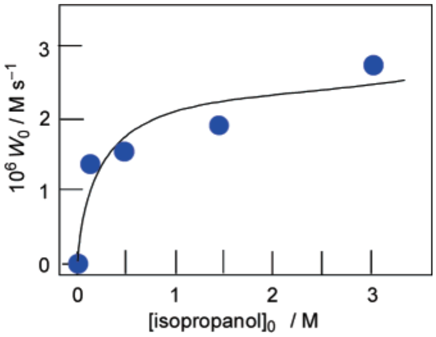


Figure 19. Dependence of the initial rate of acetone accumulation in the isopropanol oxidation in acetonitrile solution under UV ($\lambda \geq 253$ nm) irradiation on the initial concentration of isopropanol. Conditions: $[H_2O_2]_0 = 0.50$ M; $[H_2O] = 2.2$ M; 20 °C.

and 11d) and in the photolysis of H_2O_2 (refs 28) are similar: $k(CH_3CN)/k(Me_2CH{-}OH) = 0.0083$ and 0.013, respectively. Both these observations are in agreement with the conclusion that the oxidizing species that operates in acetonitrile is the hydroxyl radical. Analysis of the data presented in Figure 17 opens the possibility to determine the ratio of rate constants for the hydroxyl radical interactions with acetonitrile and isopropanol, which turned out to be 0.012. Calculated with use of this constant ratio, the dependence of the acetone accumulation rate on the initial concentration of isopropanol is presented in Figure 17 as a dotted curve, showing a good agreement with the experimental data.

Figure 19 presents the results of photochemical experiments that measured the rate of acetone formation in acetonitrile at various concentrations of isopropanol. This dependence of W_0 on $[Me_2CH{-}OH]_0$ also corresponds to the competition between acetonitrile and isopropanol for hydroxyl radicals. The estimation of the ratio of the rate constants for these two reactions gave the following value: $k(HO^\bullet + CH_3CN)/k(HO^\bullet + Me_2CH{-}OH) = 0.008$. It is clear that in this case we have also a good agreement with ratios obtained for other systems. These results demonstrate also that reactivities of cyclohexane and isopropanol toward hydroxyl radicals are close. This allows us to assume that, like in acetonitrile, the oxidizing species in isopropanol is also the hydroxyl radical. It should be noted that there is information in the literature on rate constants for the interactions of hydroxyl radicals with acetonitrile, isopropanol, and cyclohexane. However, the variation of these values is rather substantial for different sources. Thus, the following parameters can be found: 3.6×10^6 and 2.2×10^7 M^{-1} s^{-1} for acetonitrile,[29a] 1.26×10^9 and 3×10^8 M^{-1} s^{-1} for cyclohexane,[29b,c] and $(1.7{-}2.2) \times 10^9$ M^{-1} s^{-1} for isopropanol.[29d] Taking into account the fact that the variation of these values is lowest in the case of isopropanol and using the results of our own determinations described above (we assume that $k(HO^\bullet + Me_2CH{-}OH) = 1.9 \times 10^9$ M^{-1} s^{-1}), we can calculate the following constants: $k(HO^\bullet + CH_3CN) = (1.5{-}2.3) \times 10^7$ M^{-1} s^{-1} and $k(HO^\bullet + CyH) = (1.1{-}1.9) \times 10^9$ M^{-1} s^{-1}.

The catalytic reagents "vanadate$-H_2O_2-$PCA" in isopropanol and acetonitrile are similar not only because in both cases hydroxyl radicals are the oxidizing species but also because the modes of dependences of W_0 on the initial concentration of H_2O_2 are the same (compare Figures 15 and 20). At a low concentration of hydrogen peroxide, the order of the reaction rate relative to $[H_2O_2]_0$ is higher than first order. However, it is close to first order under those concentrations of hydrogen peroxide when, in accordance with electronic spectroscopy, the most of vanadium is present in the form of a monoperoxo complex. Some decrease in the order of the reaction rate toward hydrogen peroxide (which has been detected at high concentrations of H_2O_2) correlates with a decrease of the content of vanadium existing in the form of a spectroscopically registered monoperoxo complex. The mode of the dependence of W_0 on $[H_2O_2]_0$ is in agreement with our assumption about the participation of a vanadium diperoxo complex in the rate-limiting step generating hydroxyl radicals.

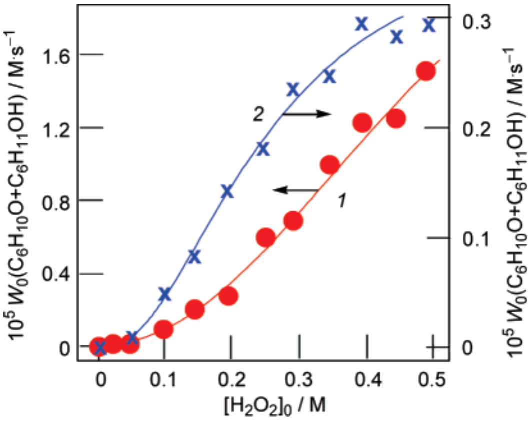


Figure 20. Dependences of the initial rate of cyclohexane oxidation in MeCN on the initial concentration of H_2O_2. Conditions: $[H_2O] = 2.2$ M; 40 °C. Curve 1: $[n\text{-}Bu_4NVO_3]_0 = 0.5$ mM; $[PCA]_0 = 2$ mM; $[MeCN]_0 = 17.2$ M; $[\text{cyclohexane}]_0 = 0.46$ M. Curve 2: $[n\text{-}Bu_4NVO_3]_0 = 0.1$ mM; $[PCA]_0 = 0.4$ mM; $[MeCN]_0 = 17.7$ M; $[\text{cyclohexane}]_0 = 0.20$ M.

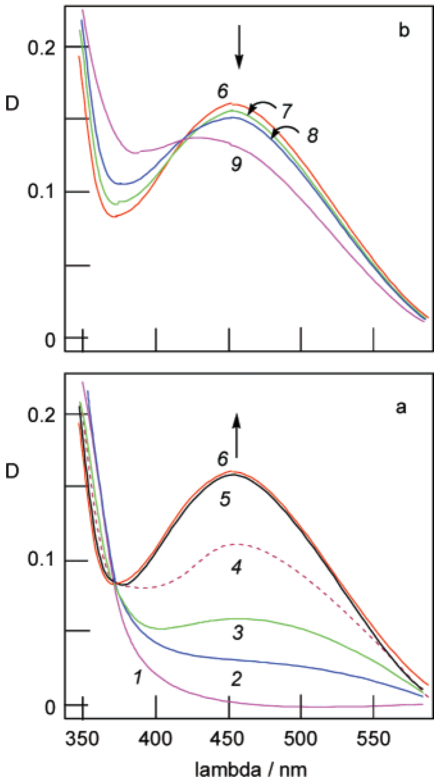
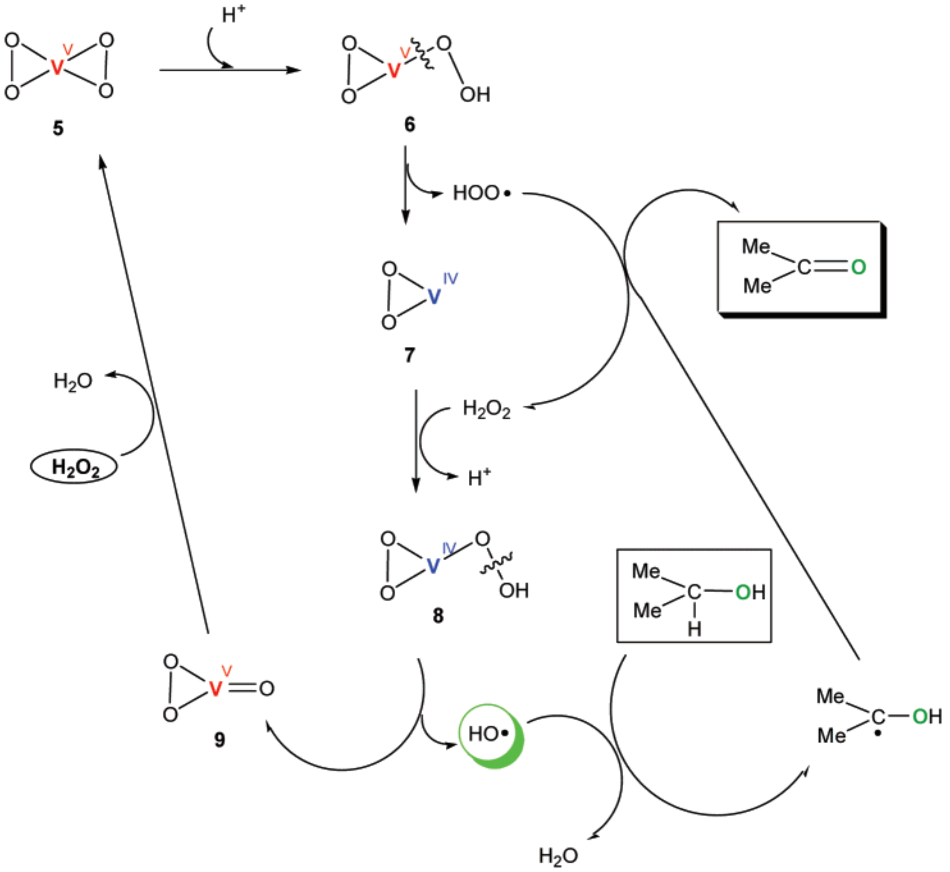


Figure 21. Electronic spectra of the solution of $n\text{-}Bu_4NVO_3$ (0.5 mM) and PCA (2 mM) in MeCN containing water (2.2 M) at various concentrations of added H_2O_2: 0.0 (1), 0.0002 (2), 0.0004 (3), 0.0010 (4), 0.0020 (5), 0.0040 (6), 0.024 (7), 0.25 (8), 0.50 (9) M. Components were mixed in a cuvette, and after 2 min the spectra were taken (40 °C).

We found also that, under the same conditions, the rates of acetone formation in isopropanol and cyclohexane oxidation in acetonitrile are close (compare Figures 17 and 18). In addition, in both systems at the same concentrations, we observe an absorption at 457 nm due to a monoperoxo complex containing

SCHEME 1 A Simplified Catalytic Cycle Proposed for 2-Propanol Oxidation without Participation of Atmospheric Oxygen



pca ligands. The behavior of the D_{457} value in both isopropanol and acetonitrile is essentially the same (compare Figures 9 and 21). These results suggest that the mechanisms of generation of the oxidizing species in both solvents are similar. Moreover, on the one hand, the equilibrium constants of the peroxo complex formation and, on the other hand, the constants of the rate-limiting decomposition of the diperoxo complexes are close. These results, the peculiarities of concentration changes for peroxo complexes in acetonitrile observed in the present work, and the calculations made by Bell and co-workers[15] prompted us to modify our understanding[10l,11d] of the reagent behavior in acetonitrile.

Thus, we may conclude that both the isopropanol oxidation in isopropanol and the alkane oxidation in acetonitrile proceed via similar routes. The rate-limiting step is apparently the monomolecular decomposition of a diperoxo vanadium complex containing one pca ligand. This decomposition is accompanied by the electron transfer from the peroxo ligand to the V(V) complex and by the formation of a peroxy radical and a V(IV) derivative

$$\text{“}(H_2O_2)(PCA)V^{V}(H_2O_2)\text{”} \rightarrow \text{“}(H_2O_2)(PCA)V^{IV}\text{”} + H^+ + HOO^{\bullet} \quad (28)$$

or in more simple form

$$\text{“}V^{V}\text{”} + H_2O_2 \rightarrow \text{“}V^{IV}\text{”} + H^+ + HOO^{\bullet} \quad (28a)$$

Previously[10l,11d] we treated the decomposition of a monoperoxo vanadium(V) complex according to this scheme. However, the results obtained in the present work allow us to propose that it is the diperoxo complex that is involved into such a decomposition. The interaction of the vanadium(IV) derivative with a new hydrogen peroxide molecule (possibly to produce a new diperoxo complex) leads to hydroxyl radical generation

$$\text{“}(H_2O_2)(PCA)V^{IV}\text{”} + H_2O_2 \rightarrow \text{“}(H_2O_2)(PCA)V^{V}\text{”} + HO^- + HO^{\bullet} \quad (29)$$

or in more simple form

$$\text{“}V^{IV}\text{”} + H_2O_2 \rightarrow \text{“}V^{V}\text{”} + HO^- + HO^{\bullet} \quad (29a)$$

A slightly different mechanism of radical generation also can be proposed. According to this mechanism, a diperoxovanadium(V) complex decomposes with simultaneous participation of the two peroxo ligands. In this case one molecule of the diperoxovanadium(V) complex generates both peroxyl and hydroxyl radical, either simultaneously or via two consecutive steps

$$\text{“}(H_2O_2)(PCA)V^{V}(H_2O_2)\text{”} \rightarrow \text{“}(PCA)V^{V}\text{”} + H^+ + HOO^{\bullet} + HO^- + HO^{\bullet} \quad (30)$$

As it has been mentioned above, recent calculations by Bell and co-workers[15] showed that it is the diperoxo complex that decomposes in the catalytic alkane oxidation with participation of the “H_2O_2−vanadium derivative−PCA” reagent in acetonitrile. It was concluded that the $HOO^{\bullet}$ radical cannot be produced as a result of a V−OOH bond cleavage in the complex formed directly from the precursors, because the activation barrier for this process is too high. However, $HOO^{\bullet}$ radicals are formed via a sequence of additional steps involving lower activation barriers. It is noteworthy that Bell and co-workers[15] found that these are two of the most energetically favorable reactions. The first one is decomposition of the (pca)V(OH)(OO)(OOH) species (structure **12** in ref 15, i.e., the diperoxo complex) with participation of an acetonitrile molecule (reaction 11 in ref 15) in accord with equation

$$\mathrm{(pca)V(OH)(OO)(OOH) + MeCN \rightarrow (pca)V(OH)(OO)(NCMe) + HOO^{\bullet}} \quad (31)$$

The second process is decomposition of the (pca)V(OO)-$(OOH)_2$ species (structure **17** in ref 15, in which the OO fragment is a monodentate ligand) without participation of acetonitrile (reaction 11 in ref 15) as shown below

$$\mathrm{(pca)V(OO)(OOH)_2 \rightarrow (pca)V(OO)(OHO) + HOO^{\bullet}} \quad (32)$$

It is useful to repeat here that the *kinetically* rate-limiting step of the reaction is the monomolecular decomposition of diperoxovanadium complex. In reality, the decomposition of the species "$V(H_2O_2)_2$(pca)", which is accompanied by the active radical generation, can occur via a sequence of a few steps. One of these steps can be the migration of hydrogen from a coordinated hydrogen peroxide molecule to the oxygen of a pca ligand at a vanadium center. In accordance with our assumption[10l] and calculations by Bell and co-workers[15] the hydrogen transfer is the step that determines the rate of the monomolecular decomposition of "$V(H_2O_2)_2$(pca)" and totally the rate of the overall process. The vanadium derivative thus formed reacts further with new hydrogen peroxide molecules transforming into the active diperoxo complex.

In the next step in the case of the alcohol, the hydroxyl radical abstracts the hydrogen atom

$$\mathrm{HO^{\bullet} + Me_2CH(OH) \rightarrow H_2O + Me_2C^{\bullet}(OH)} \quad (33)$$

and the radical produced from isopropanol (at least in a formal scheme) can react with the peroxyl radical generated in reaction 28 or 30 affording the oxidation product (acetone) and a hydrogen peroxide molecule

$$\mathrm{Me_2C^{\bullet}(OH) + HOO^{\bullet} \rightarrow Me_2C{=}O + HOOH} \quad (34)$$

The catalytic cycle becomes now closed (Scheme 1), and it is clear that for the oxidation of isopropanol in the absence of atmospheric oxygen the system requires one hydrogen peroxide molecule to produce one acetone molecule.

The alkane oxygenation terminates in a somewhat different way. The hydroxyl radical abstracts the hydrogen atom from the cyclohexane (reaction 35) and the alkyl radical thus formed reacts rapidly with an oxygen molecule (reaction 36). To close the cycle formally we can introduce reaction 37, which affords cyclohexyl hydroperoxide as a product. It can be seen that in this oxidation the system requires two hydrogen peroxide molecules per one hydrocarbon molecule.[10l] In accordance with reactions 35−37 the second step requires the dioxygen molecule whereas in (formally introduced into the cycle) reaction 37 dioxygen is evolved

$$\mathrm{HO^{\bullet} + CyH \rightarrow H_2O + Cy^{\bullet}} \quad (35)$$

$$\mathrm{Cy^{\bullet} + O_2 \rightarrow CyOO^{\bullet}} \quad (36)$$

$$\mathrm{CyOO^{\bullet} + HOO^{\bullet} \rightarrow CyOOH + O_2} \quad (37)$$

Conclusions

In this work we have demonstrated that the oxidations of 2-propanol in 2-propanol and alkanes in acetonitrile by the "H_2O_2−vanadate anion−PCA" reagent proceed via the same mechanism. This mechanism involves the formation of a diperoxovanadium(V) complex containing a pca ligand, which decomposes to produce peroxyl radical and then hydroxyl radical. The latter attacks the substrate and stimulates its oxidation.

Acknowledgment. This work was supported by the Russian Basic Research Foundation (Grant No. 06-03-32344-a) and the Swiss National Science Foundation. The authors thank also 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").

Supporting Information Available: ^{51}V NMR spectrum of n-Bu_4NVO_3 in isopropanol containing water, ^{1}H NMR spectra of n-Bu_4NVO_3 in CD_3CN, ^{1}H NMR spectra of n-Bu_4NVO_3 + PCA, n-Bu_4NVO_3 + PCA + H_2O, and PCA, ^{51}V NMR spectrum of NH_4VO_3 + PCA, electronic spectra of the solution of PCA and H_2O_2 in isopropanol containing water at various concentrations of added n-Bu_4NVO_3, and electronic spectra of the solution of n-Bu_4NVO_3 and PCA in isopropanol containing water at various concentrations of added H_2O_2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625−638. (b) Conte, V.; Di Furia, F.; Licini, G. *Appl. Catal., A* **1997**, *157*, 335−361. (c) *Vanadium Compounds: Chemistry, Biochemistry, and Therapeutic Applications*; Tracey, A. S., Crans, D. C. Eds.; ACS Symposium Series 711; American Chemical Society: Washington, DC, 1998. (d) Bolm, C. *Coord. Chem. Rev.* **2003**, *237*, 245−256. (e) Brégeault, J.-M. *J. Chem. Soc., Dalton Trans.* **2003**, 3289−3302. (f) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849−902. (g) Brégeault, J.-M.; Vennat, M.; Salles, L.; Piquemal, J.-Y.; Yahdih Mahha, Y.; Briot, E.; Bakala, P. C.; Atlamsani, A.; Thouvenot, R. *J. Mol. Catal. A: Chem.* **2006**, *250*, 177−189.

(2) Recent publications on the oxidation of alkanes: (a) Kozlov, A.; Asakura, K.; Iwasawa, Y. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 809−816. (b) Kozlov, A.; Kozlova, A.; Asakura, K.; Iwasawa, Y. *J. Mol. Catal. A: Chem.* **1999**, *137*, 223−237. (c) Reis, P. M.; Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Chem. Commun.* **2000**, 1845−1846. (d) Süss-Fink, G.; Stanislas, S.; Shul'pin, G. B.; Nizova, G. V. *Appl. Organomet. Chem.* **2000**, *14*, 623−628. (e) Gekhman, E. E.; Stolyarov, I. P.; Ershova, N. V.; Moiseeva, N. I.; Moiseev, I. I. *Dokl. Akad. Nauk* **2001**, *378*, 639−643 (in Russian). (f) Süss-Fink, G.; Gonzalez, L.; Shul'pin, G. B. *Appl. Catal., A* **2001**, *217*, 111−117. (g) Mishra, G. S.; Kumar, A. *J. Mol. Catal. A: Chem.* **2003**, *192*, 275−280. (h) Mishra, G. S.; Kumar, A. *React. Kinet. Catal. Lett.* **2003**, *80*, 223−231. (i) Pillai, U. R.; Sahle-Demessie, E. *New J. Chem.* **2003**, *27*, 525−528. (j) Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Fraústo da Silva, J. J. R.; Kitamura, T.; Fujiwara, Y.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 821−823. (k) Shul'pin, G. B.; Kozlov, Y. N. *Org. Biomol. Chem.* **2003**, *1*, 2303−2306. (l) Joseph, T.; Hartmann, M.; Ernst, S.; Halligudi, S. B. *J. Mol. Catal. A: Chem.* **2004**, *207*, 129−135. (m) Si, T. K.; Chowdhury, K.; Mukherjee, M.; Bera, D. C.; Bhattacharyya, R. *J. Mol. Catal. A: Chem.* **2004**, *219*, 241−247. (n) Mishra, G. S.; Pombeiro, A. J. L. *J. Mol. Catal. A: Chem.* **2005**, *239*, 96−102. (o) Gonzalez Cuervo, L.; Kozlov, Y. N.; Süss-Fink, G.; Shul'pin, G. B. *J. Mol. Catal. A: Chem.* **2004**, *218*, 171−177. (p) Mishra, G. S.; Pombeiro, A. J. L. *Appl. Catal., A* **2006**, *304*, 185−194. (r) Shetti, V. N.; Rani, M. J.; Srinivas, D.; Ratnasamy, P. *J. Phys. Chem. B* **2006**, *110*, 677−679. Oxidative carboxylation of alkanes: (q) Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Catal.* **2005**, *235*, 333−340.

(3) Hydroxylation of arenes: (a) Ishida, M.; Masumoto, Y.; Hamada, R.; Nishiyama, S.; Tsuruya, S.; Masai, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 847−853. (b) Masumoto, Y.; Hamada, R.; Yokota, K.; Nishiyama,

S.; Tsuruya, S. *J. Mol. Catal. A: Chem.* **2002**, *184*, 215−222. (c) Lemke, K.; Ehrich, H.; Lohse, U.; Berndt, H.; Jähnisch, K. *Appl. Catal., A* **2003**, *243*, 41−51. (d) Shul'pin, G. B.; Lachter, E. R. *J. Mol. Catal. A: Chem.* **2003**, *197*, 65−71. (e) Reis, P. M.; Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Mol. Catal. A: Chem.* **2004**, *224*, 189−195. (f) Zhang, J.; Tang, Y.; Li, G.; Hu, C. *Appl. Catal., A* **2005**, *278*, 251−261. (g) Jian, M.; Zhu, L.; Wang, J.; Zhang, J.; Li, G.; Hu, C. *J. Mol. Catal. A: Chem.* **2006**, *253*, 1−7.

(4) Oxidation of phenols: (a) Seelan, S.; Sinha, A. K. *Appl. Catal., A* **2003**, *238*, 201−209. (b) Yin, C.-X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 9003−9013. (c) Yu, J.; Yang, P.; Yang, Y.; Wu, T.; Parquette, J. R. *Catal. Commun.* **2006**, *7*, 153−156.

(5) Epoxidation of olefins: (a) Bühl, M.; Schurhammer, R.; Imhof, P. *J. Am. Chem. Soc.* **2004**, *126*, 3310−3320. (b) Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5136−5141. (c) Maurya, M. R.; Kumar, A. *J. Mol. Catal. A: Chem.* **2006**, *250*, 190−198. (d) Mizuno, N.; Nakagawa, Y.; Yamaguchi, K. *J. Mol. Catal. A: Chem.* **2006**, *251*, 336−342.

(6) Oxidation of phosphines and sulfides: (a) Du, G.; Espenson, J. H. *Inorg. Chem.* **2005**, *44*, 2465−2471. (b) Hinch, M.; Jacques, O.; Drago, C.; Caggiano, L.; Jackson, R. F. W.; Dexter, C.; Anson, M. S.; Macdonald, S. J. F. *J. Mol. Catal. A: Chem.* **2006**, *251*, 123−128.

(7) Biological and biomimetic processes: (a) Crans, D. C.; Yang, L.; Jakusch, T.; Kiss, T. *Inorg. Chem.* **2000**, *39*, 4409−4416. (b) Sam, M.; Hwang, J. H.; Chanfreau, G.; Abu-Omar, M. M. *Inorg. Chem.* **2004**, *43*, 8447−8455. (c) Kravitz, J. Y.; Pecoraro, V. L.; Carlson, H. A. *J. Chem. Theory Comput.* **2005**, *1*, 1265−1274. (d) Raugei, S.; Carloni, P. *J. Phys. Chem. B* **2006**, *110*, 3747−3758. (e) Wilkins, P. C.; Johnson, M. D.; Holder, A. A.; Crans, D. C. *Inorg. Chem.* **2006**, *45*, 1471−1479. (f) Borden, J.; Crans, D. C.; Florián, J. *J. Phys. Chem. B* **2006**, *110*, 14988−14999. (g) Zhang, Y.; Yang, X.-D.; Wang, K.; Crans, D. C. *J. Inorg. Biochem.* **2006**, *100*, 80−87.

(8) Oxidation of alcohols: (a) Bonchio, M.; Bortolini, O.; Carraro, M.; Conte, V.; Primon, S. *J. Inorg. Biochem.* **2000**, *80*, 191−194. (b) Bonchio, M.; Bortolini, O.; Conte, V.; Primon, S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 763−765. (c) Li, C.; Zheng, P.; Li, J.; Zhang, H.; Cui, Y.; Shao, Q.; Ji, X.; Zhang, J.; Zhao, P.; Xu, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 5063−5066. (d) Manyar, H. G.; Chaure, G. S.; Kumar, A. *J. Mol. Catal. A: Chem.* **2006**, *243*, 244−252.

(9) (a) Cundari, T. R.; Sisterhen, L. L.; Stylianopoulos, C. *Inorg. Chem.* **1997**, *36*, 4029−4034. (b) Hwang, J. H.; Larson, R. K.; Abu-Omar, M. M. *Inorg. Chem.* **2003**, *42*, 7967−7977. (c) Du, G.; Espenson, J. H. *Inorg. Chem.* **2005**, *44*, 5514−5522. (d) Bühl, M. *Inorg. Chem.* **2005**, *44*, 6277−6283. (e) Yu, X.-Y.; Cai, S.-H.; Xu, X.; Chen, Z. *Inorg. Chem.* **2005**, *44*, 6755−6762. (f) Tatiersky, J.; Schwendt, P.; Sivák, M.; Marek, J. *J. Chem. Soc., Dalton Trans.* **2005**, 2305−2311. (g) Maurya, M. R.; Agarwal, S.; Bader, C.; Rehder, D. *Eur. J. Inorg. Chem.* **2005**, 147−157. (h) Garribba, E.; Lodyga-Chruscinska, E.; Micera, G.; Panzanelli, A.; Sanna, D. *Eur. J. Inorg. Chem.* **2005**, 1369−1382. (i) Nica, S.; Pohlmann, A.; Plass, W. *Eur. J. Inorg. Chem.* **2005**, 2032−2036. (j) Maurya, M. R.; Kumar, A.; Bhat, A. R.; Azam, A.; Bader, C.; Rehder, D. *Inorg. Chem.* **2006**, *45*, 1260−1269.

(10) (a) Shul'pin, G. B.; Attanasio, D.; Suber, L. *Russ. Chem. Bull.* **1993**, *42*, 55−59. (b) Shul'pin, G. B.; Druzhinina, A. N.; Nizova, G. V. *Russ. Chem. Bull.* **1993**, *42*, 1327−1329. (c) Nizova, G. V.; Shul'pin, G. B. *Russ. Chem. Bull.* **1994**, *43*, 1146−1148. (d) Shul'pin, G. B.; Süss-Fink G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1459−1463. (e) Shul'pin, G. B.; Drago, R. S.; Gonzalez, M. *Russ. Chem. Bull.* **1996**, *45*, 2386−2388. (f) Guerreiro, M. C.; Schuchardt, U.; Shul'pin, G. B. *Russ. Chem. Bull.* **1997**, *46*, 749−754. (g) Shul'pin, G. B.; Guerreiro, M. C.; Schuchardt, U. *Tetrahedron* **1996**, *52*, 13051−13062. (h) Nizova, G. V.; Süss-Fink, G.; Shul'pin, G. B. *Tetrahedron* **1997**, *53*, 3603−3614. (i) Schuchardt, U.; Guerreiro, M. C.; Shul'pin, G. B. *Russ. Chem. Bull.* **1998**, *47*, 247−252. (j) Süss-Fink, G.; Nizova, G. V.; Stanislas, S.; Shul'pin, G. B. *J. Mol. Catal. A: Chem.* **1998**, *130*, 163−170. (k) Shul'pin, G. B.; Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Russ. Chem. Bull.* **1999**, *48*, 887−890. (l) Shul'pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1351−1371. (m) de la Cruz, M. H. C.; Kozlov, Y. N.; Lachter, E. R.; Shul'pin, G. B. *New J. Chem.* **2003**, *27*, 634−638. (n) Kozlov, Y. N.; Nizova, G. V.; Shul'pin, G. B. *J. Mol. Catal. A: Chem.* **2005**, *227*, 247−253. (o) Jannini, M. J. D. M.; Shul'pina, L. S.; Schuchardt, U.; Shul'pin, G. B. *Petrol. Chem.* **2005**, *45*, 413−418.

(11) (a) Shul'pin, G. B.; Attanasio, D.; Suber, L. *J. Catal.* **1993**, *142*, 147−152. (b) Nizova, G. V.; Süss-Fink, G.; Shul'pin, G. B. *Chem. Commun.* **1997**, 397−398. (c) Süss-Fink, G.; Stanislas, S.; Shul'pin, G. B.; Nizova, G. V. *Appl. Organomet. Chem.* **2000**, *14*, 623−628. (d) Kozlov, Y. N.; Nizova, G. V.; Shul'pin, G. B. *Russ. J. Phys. Chem.* **2001**, *75*, 770−774. (e) Nizova, G. V.; Kozlov, Y. N.; Shul'pin, G. B. *Russ. Chem. Bull.* **2004**, 2330−2333.

(12) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. (b) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000. (c) Shul'pin, G. B. *J. Mol. Catal. A: Chem.* **2002**, *189*, 39−66. (d) Shul'pin, G. B. *C. R. Chim.* **2003**, *6*, 163−178. (e) Shul'pin, G. B. Oxidations of C−H compounds catalyzed by metal complexes. In *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, Chapter 2.2, pp 215−242.

(13) (a) Süss-Fink, G.; Yan, H.; Nizova, G. V.; Stanislas, S.; Shul'pin, G. B. *Russ. Chem. Bull.* **1997**, *46*, 1801−1803. (b) Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Shul'pin, G. B. *Chem. Commun.* **1998**, 1885−1886. (c) Süss-Fink, G.; Stanislas, S.; Shul'pin, G. B.; Nizova, G. V.; Stoeckli-Evans, H.; Neels, A.; Bobillier, C.; Claude, S. *J. Chem. Soc., Dalton Trans.* **1999**, 3169−3175. (d) Süss-Fink, G.; Gonzalez Cuervo, L.; Therrien, B.; Stoeckli-Evans, H.; Shul'pin, G. B. *Inorg. Chim. Acta* **2004**, *357*, 475−484.

(14) (a) Fickl, H.; Theron, A. J.; Grimmer, H.; Oommen, J.; Ramafi, G. J.; Steel, H. C.; Visser, S. S.; Anderson, R. *Free Radical Biol. Med.* **2006**, *40*, 146−155. (b) Ścibior, A.; Zaporowska, H.; Ostrowski, J.; Banach, A. *Chem.-Biol. Interact.* **2006**, *159*, 213−222.

(15) Khaliullin, R. Z.; Bell, A. T.; Head-Gordon, M. *J. Phys. Chem. B* **2005**, *109*, 17984−17992.

(16) (a) Gran, G. *Acta Chem. Scand.* **1950**, *4*, 559−564. (b) Irving, H. M.; Miles, M. G.; Pettit, L. D. *Anal. Chim. Acta* **1967**, *38*, 475−488. (c) Zékány, L.; Nagypál, I. In *Computational Methods for the Determination of Stability Constants*; Leggett, D. L., Ed.; Plenum Press: New York, 1985, p 291. (d) Pettersson, L.; Hedman, B.; Anderson, I.; Ingri, N. *Chem. Scr.* **1983**, *22*, 254−264.

(17) (a) Shul'pin, G. B.; Druzhinina, A. N. *React. Kinet. Catal. Lett.* **1992**, *47*, 207−211. (b) Shul'pin, G. B.; Nizova, G. V. *React. Kinet. Catal. Lett.* **1992**, *48*, 333−338. (c) Shul'pin, G. B.; Bochkova, M. M.; Nizova, G. V. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1465−1469. (d) Shul'pin, G. B.; Nizova, G. V.; Kozlov, Y. N. *New J. Chem.* **1996**, *20*, 1243−1256.

(18) (a) Elvingson, K.; Crans, D. C.; Pettersson, L. *J. Am. Chem. Soc.* **1997**, *119*, 7005−7012. (b) Sanna, D.; Micera, G.; Buglyó, P.; Kiss, T.; Gajda, T.; Surdy, P. *Inorg. Chim. Acta* **1998**, *268*, 297−305. (c) Anderson, I.; Gorzsás, A.; Pettersson, L. *J. Chem. Soc., Dalton Trans.* **2004**, 421−428. (d) Buglyó, P.; Crans, D. C.; Nagy, E. M.; Lindo, R. L.; Yang, L.; Smee, J. J.; Jin, W.; Chi, L.-H.; Godzala, M. E., III.; Willsky, G. R. *Inorg. Chem.* **2005**, *44*, 5416−5427.

(19) (a) Yun, S.; Kim, I.; Kim, Y. *Thermochim. Acta* **1990**, *162*, 341−345. (b) Napoli, A.; Margi, A. *Ann. Chim. (Rome)* **1989**, *79*, 93−104.

(20) (a) Rehder, D. *Z. Naturforsch., B: Chem. Sci.* **1977**, *32*, 771−775. (b) Paulsen, K.; Rehder, D. *Z. Naturforsch., A: Phys. Sci.* **1982**, *37*, 139−149. (c) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058−3062.

(21) In a recent paper, Bell and co-workers[15] suggested that vanadate−PCA solutions in acetonitrile, even at high PCA concentrations, contain a mixture of a mono-adduct and of a bis-adduct rather than only the bis-adduct $[VO_2(pca)_2]^-$ that we had previously assumed.[10l] The presence of only one set of aromatic ^{1}H NMR signals generated by coordinated PCA was explained by indistinguishable ^{1}H NMR spectra of mono- and bis-pca complexes.[15] However, this hypothesis contradicts the experimental results obtained for vanadate−PCA mixtures at different PCA:V ratios in CD_3CN (Figure S2 of the Supporting Information). At low PCA concentrations, we observed two well-resolved sets of ^{1}H NMR signals for coordinated pca ligands: one from a mono-adduct and the second from a bis-adduct. (The difference of the chemical shifts reaches 0.3 ppm.) The mono-adduct dominates at PCA:V $\leq$ 0.75:1. However, at higher PCA concentrations, its relative concentration rapidly diminishes, and the bis-adduct becomes the only PCA complex at PCA:V $>$ 2:1.

(22) Interestingly, the ^{51}V NMR spectrum of V/PCA mixtures in water reveals at least three resonances of comparable intensities in the same region of chemical shifts (Figure S4 of the Supporting Information). According to the speciation analysis described above (see section 3.2), in aqueous solutions we can expect to see not only the anion $[VO_2(pca)_2]^-$ but also some products of ligand exchange with water. As it follows from Figure S4 of the Supporting Information, this ligand exchange occurs slowly on the NMR time scale. We did not perform a detailed NMR study of products formed in the presence of H_2O_2 in aqueous solutions, because this was beyond the scope of this work.

(23) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(24) Conte, V.; Di Furia, F.; Moro, S. *Inorg. Chim. Acta* **1998**, *272*, 62−67.

(25) (a) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1173−1177. (b) Jaswal, J. S.; Tracey, A. S. *Inorg. Chem.* **1991**, *30*, 3718−3722.

(26) Vanadium alkoxo complexes have been studied inter alia with ^{51}V and ^{1}H NMR methods in works by Talsi and co-workers: (a) Talsi, E. P.; Chinakov, V. D.; Babenko, V. P.; Zamaraev, K. I. *J. Mol. Catal.* **1993**, *81*, 235−254. (b) Talsi, E. P.; Shalyaev, K. V. *J. Mol. Catal.* **1994**, *92*, 245−255. For vanadium alkoxides, see: (c) Kempf, J. Y.; Maigret, B.; Crans,

D. C. *Inorg. Chem.* **1996**, *35*, 6485−6494. For oxovanadium(V) triethanolamine complex (vanadatrane) and similar compounds, see: (d) Voronkov, M. G.; Osipov, O. A.; Kogan, V. A. Chetverikov, V. A.; Lapsin, A. F. *Khim. Geterotsikl. Soedin.* **1967**, 35−38 (in Russian). (e). Crans, D. C.; Chen, H.; Anderson, O. P.; Miller, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 6769−6776. (f) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 6142−6148.

(27) (a) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1990**, *29*, 4457−4461. (b) Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1995**, *117*, 3475−3484.

(28) (a) Kozlov, Y. N.; Gonzalez-Cuervo, L.; Süss-Fink, G.; Shul'pin, G. B. *Russ. J. Phys. Chem.* **2003**, *77*, 575−579. (b) Shul'pin, G. B.; Nizova, G. V.; Kozlov, Y. N.; Gonzalez Cuervo, L., Süss-Fink, G. *Adv. Synth. Catal.* **2004**, *346*, 317−332.

(29) (a) Farhataziz; Ross, A. B. *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions*; NSRDS-NBS 59; National Bureau of Standards: Washington DC, 1977. (b) Rudakov, E. S.; Volkova, L. K.; Tretyakov, V. P. *Soobsch. Kinet. Katal.* **1981**, *16*, 333 (in Russian). (c) Khar'kova, T. V.; Arest-Yakubovich, I. L.; Lipes, V. V. *Kinet. Katal.* **1989**, *30*, 954 (in Russian). (d) Dorfman, L. M.; Adams, G. E. *Reactivity of the Hydroxyl Radical in Aqueous Solutions*; NSRDS-NBS 46; National Bureau of Standards: Washington DC, 1973, p 24.