

CHEMICAL KINETICS  
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# The Kinetics and Mechanism of Oxidation of Isopropanol with the Hydrogen Peroxide–Vanadate Ion–Pyrazine-2-Carboxylic Acid System

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**Abstract**—The vanadate anion in the presence of pyrazine-2-carboxylic acid (PCA) was found to effectively catalyze the oxidation of isopropanol to acetone with hydrogen peroxide. The electronic spectra of solutions and the kinetics of oxidation were studied. The conclusion was drawn that the rate-determining stage of the reaction was the decomposition of the vanadium(V) diperoxo complex with PCA, and the particle that induced the oxidation of isopropanol was the hydroxyl radical. Supposedly, the HO· radical detached a hydrogen atom from isopropanol, and the Me<sub>2</sub>C·(OH) radical formed reacted with HOO· to produce acetone and hydrogen peroxide. The electronic spectra of solutions in isopropanol and acetonitrile and the dependences of the initial rates of isopropanol oxidation without a solvent and cyclohexane oxidation in acetonitrile on the initial concentration of hydrogen peroxide were compared. The conclusion was drawn that hydroxyl radicals appeared in the oxidation of alkanes in acetonitrile in the decomposition of the vanadium diperoxo complex rather than the monoperoxo derivative, as was suggested by us earlier.

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## INTRODUCTION

We found earlier that the VO<sub>3</sub><sup>-</sup> vanadate anion effectively catalyzed the oxidation of saturated and aromatic hydrocarbons with hydrogen peroxide in acetonitrile in air at temperatures of from 20 to 70°C [1–18]. The necessary condition for the reaction to occur was the presence of pyrazine-2-carboxylic acid (PCA) as a cocatalyst in concentrations several times higher than the concentration of the vanadium complex. The primary products of the oxidation of alkanes were alkylhydroperoxides, which decomposed during the reaction to the corresponding carbonyl compound (ketone or aldehyde) and alcohol. At the initial stage of the reaction, especially at a low temperature, only alkylhydroperoxides were detected in solutions. Benzene was transformed into phenol. A study of the selectivity of oxidation of various alkanes showed that the oxidative action of the system under consideration was caused by the generation of hydroxyl radicals, which attacked hydrocarbon C–H bonds [13, 14].

According to [14], pyrazinecarboxylic acid facilitated proton transfer between separate ligands in the coordination sphere of vanadium and thereby accelerated the decomposition of the vanadium peroxo complex with PCA. This increased the rate of the generation of hydroxyl radicals. Recently, this system was studied theoretically by the density functional theory (DFT) method [19]. It was shown that, indeed, direct proton

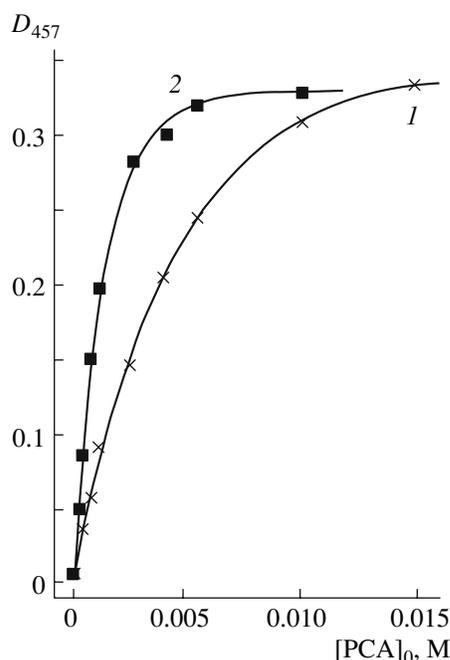
transfer from the H<sub>2</sub>O<sub>2</sub> molecule to the oxygen atom of the vanadium-containing particle required overcoming a barrier much higher than when a proton migrated from hydrogen peroxide first to the carboxyl group of the pyrazine-2-carboxylic acid anion (coordinated to the vanadium ion at the nitrogen atom) and then to the V=O fragment.

In this work, we for the first time studied the mechanism of oxidation of isopropanol in the system specified by spectral and kinetic methods. Oxidation was performed in the substrate itself as a solvent and in acetonitrile. We also compared the oxidation of isopropanol with the oxygenation of cyclohexane in acetonitrile.

## EXPERIMENTAL

Oxidation reactions were performed in air in a glass cylindrical temperature-controlled vessel. The reaction solution volume was 10 ml. Reaction solution samples (0.6 ml) were taken in certain time intervals. After treatment with excess solid triphenylphosphine for 10 min, the samples were analyzed by gas-liquid chromatography. Hydrogen peroxide was introduced as a 30% aqueous solution from Fluka (not stabilized).

A DANI-86.10 chromatograph with a 25 m × 0.32 mm × 0.25 μm capillary column, a CP-WAX52CB carrier, and an SP-4400 integrator was used; the carrier gas was helium. Chromatograms were calibrated



**Fig. 1.** Dependences of the optical density of absorption  $D_{457}$  on the concentration of pyrazinecarboxylic acid added to a solution of  $n\text{-Bu}_4\text{NVO}_3$  (1 mM), water (2.2 M), and  $\text{H}_2\text{O}_2$  ((1) 0.5 M and (2) 0.004 M) in isopropanol at 50°C.

against substrates (isopropanol or cyclohexane) and oxidation products (acetone or cyclohexanol and cyclohexanone). Acetonitrile was used as an internal reference. The electronic spectra were recorded on a Uvi-con-930 spectrophotometer in quartz temperature-controlled cells (1 cm).

## RESULTS AND DISCUSSION

As with the oxidation of alkanes in acetonitrile catalyzed by vanadate ions, the oxidation of isopropanol in isopropanol as a solvent occurs at a much lower rate in the absence of pyrazinecarboxylic acid (see works on the oxidation of alcohols catalyzed by vanadium derivatives [20–26]).

We found that the addition of PCA to a solution of vanadate ions in the form of the  $n\text{Bu}_4\text{NVO}_3$  salt ( $10^{-3}$  M) and hydrogen peroxide (0.5 M) in isopropanol containing 2.2 M water resulted in the appearance of a new optical absorption band in the visible range with a maximum at 457 nm. This absorption did not appear in the absence of vanadium,  $\text{H}_2\text{O}_2$ , or PCA. It is therefore logical to relate it to the formation of a vanadium peroxy complex containing PCA in the coordination sphere. The intensity of absorption at 457 nm increased as the concentration of PCA grew, reached a maximum at  $[\text{PCA}]_0 > 10^{-2}$  M, and then virtually ceased to change (Fig. 1, curve 1). A similar picture was observed at the  $[\text{H}_2\text{O}_2]_0 = 0.004$  M concentration (Fig. 1, curve 2). Maximum optical absorption was then close to that

observed at a high concentration of  $\text{H}_2\text{O}_2$  (Fig. 1, curve 1), but the maximum was reached at a lower initial concentration of PCA ( $[\text{PCA}]_0 > 6 \times 10^{-3}$  M).

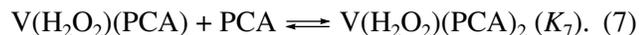
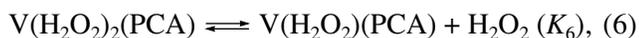
It follows that the maximum optical absorption value is virtually independent of either the concentration of  $\text{H}_2\text{O}_2$  (over the concentration range 0.004–0.5 M) or the concentration of PCA (over the concentration range 0.01–0.024 M). At the same time, it is directly proportional to the concentration of vanadate ions introduced. These data are in agreement with the suggestion that virtually all vanadium occurs in the form of the peroxy complex containing PCA in its coordination sphere under these conditions.

Changes in the optical absorption spectra of a solution of vanadate ions ( $10^{-3}$  M) and PCA ( $10^{-2}$  M) caused by the introduction of hydrogen peroxide into isopropanol containing a constant amount of water (2.2 M) show that optical absorption at 457 nm increases after the addition of small amounts of  $\text{H}_2\text{O}_2$  ( $\leq 0.004$  M), which corresponds to an increase in the concentration of the peroxyvanadium complex with PCA in the coordination sphere responsible for this band. However, already in the presence of  $\text{H}_2\text{O}_2$  in a fourfold excess over vanadate ions, an almost complete transformation of the vanadium complex with PCA into the peroxy complex is observed. The  $D_{457}$  value of the peroxy complex increases linearly over the initial portion of its dependence on the concentration of  $[\text{H}_2\text{O}_2]_0$ . We can therefore assume that the absorption observed corresponds to a monoperoxy complex. In the presence of large amounts of  $\text{H}_2\text{O}_2$  (of about 0.02–0.5 M), the concentration of the monoperoxy complex responsible for absorption at 457 nm decreases somewhat, which can be caused by its transformation into a diperoxy complex. This complex absorbs at shorter wavelengths (the isobestic point at 375 nm).

Changes in the optical density of solutions at 457 nm caused by changes in the concentration of vanadium monoperoxy complex with PCA depending on the concentration of hydrogen peroxide introduced at various PCA concentrations are shown in Fig. 2. It follows from the data obtained that the lower the concentration of PCA, the lower the concentration of hydrogen peroxide at which a maximum concentration of the monoperoxyvanadate complex is reached and the greater the extent of the conversion of this complex into the vanadium diperoxy complex at high  $\text{H}_2\text{O}_2$  concentrations (Fig. 2, curves 1, 2, and 3). These results are evidence that  $\text{H}_2\text{O}_2$  and PCA compete for coordination with vanadium.

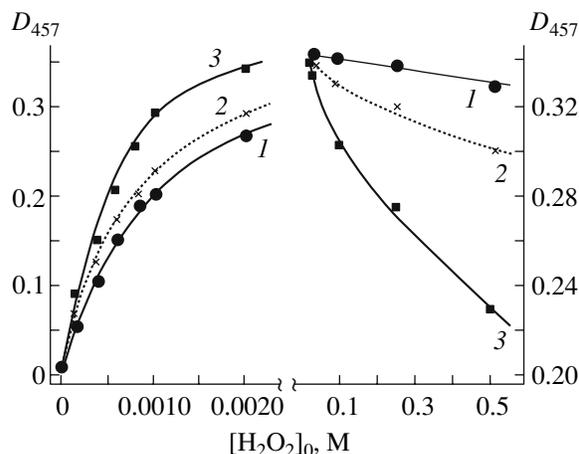
On the basis of the data described above, the equilibrium transformations of the vanadate– $\text{H}_2\text{O}_2$ –PCA system in isopropanol containing 2.2 M water can be described by the scheme





Here, we disregard the possible presence of water and/or isopropanol in the coordination sphere of vanadium because their concentrations are much higher than the concentrations of the other reagents and do not change under the conditions studied. In addition, we ignore the possibility of formation of dimeric vanadium complexes because optical absorption is directly proportional to the concentration of vanadate ions introduced under all conditions studied.

Generally, an analysis of scheme (1)–(7) requires the inclusion of three material balance equations for the concentrations of vanadate ions, hydrogen peroxide, and PCA. The resulting system of equations is fairly complex, and its correspondence to experimental data is difficult to analyze. Considering errors involved in experimental data, such an analysis is inexpedient. The situation is considerably simplified if we include the experimental data obtained at high hydrogen peroxide ( $[\text{H}_2\text{O}_2]_0/[\text{V}]_0 \geq 10$ ) and PCA ( $[\text{PCA}]_0/[\text{V}]_0 \geq 10$ ) concentrations. Their equilibrium concentrations in solution can then be considered equal to the concentrations of these reagents introduced into solutions, that is,  $[\text{H}_2\text{O}_2]_0$  and  $[\text{PCA}]_0$ , respectively, and we can take into account the material balance equation with respect to



**Fig. 2.** Dependences of  $D_{457}$  on the concentration of hydrogen peroxide added to a solution of  $n\text{-Bu}_4\text{NVO}_3$  (1 mM), water (2.2 M), and pyrazinecarboxylic acid ((1) 0.024 M, (2) 0.010 M, and (3) 0.004 M) in isopropanol at 50°C.

$[\text{V}]$  only. Because the diperoxo complex does not absorb at 457 nm, it is reasonable to assume that only the  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})$  and  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})_2$  monoperoxo complexes absorb at 457 nm. Let the absorption coefficients of these particles at 457 nm be  $\varepsilon_1$  and  $\varepsilon_2$ . Using the scheme suggested above, the optical density of the solution  $D_{457}$  at  $[\text{H}_2\text{O}_2]_0/[\text{V}]_0 \geq 10$  and  $[\text{PCA}]_0/[\text{V}]_0 \geq 10$  can be written as

$$D_{457} = K_3 K_4 K_5 K_6 [\text{H}_2\text{O}_2]_0 [\text{PCA}]_0 (\varepsilon_1 + \varepsilon_2 K_7 [\text{PCA}]_0) [\text{V}]_0 / \{1 + K_1 [\text{PCA}]_0 + K_1 K_2 [\text{PCA}]_0^2 + K_3 \{1 + K_4 K_5 K_6 [\text{PCA}]_0 (1 + K_7 [\text{PCA}]_0)\} [\text{H}_2\text{O}_2]_0 + K_3 K_4 [\text{H}_2\text{O}_2]_0^2 (1 + K_5 [\text{PCA}]_0)\}. \quad (8)$$

It follows from Fig. 2 that, at  $[\text{H}_2\text{O}_2]_0 > 0.01$  M, virtually all vanadium exists in the form of peroxo complexes with PCA. Equation (8) can then be simplified to describe the dependences shown in Fig. 2,

$$D_{457} = \frac{K_6 (\varepsilon_1 + \varepsilon_2 K_7 [\text{PCA}]_0) [\text{V}]_0}{[\text{H}_2\text{O}_2]_0 + K_6 + K_6 K_7 [\text{PCA}]_0}. \quad (9)$$

Curve 3 in Fig. 2 does not satisfy the conditions specified above because it was obtained at  $[\text{PCA}]_0/[\text{V}]_0 = 4$ . According to curves 1 and 2 in Fig. 2, the optical density decreases insignificantly as the concentration of hydrogen peroxide grows. This leads us to suggest that the  $[\text{H}_2\text{O}_2]_0$  value in the denominator in (9) is small compared with  $K_6 + K_6 K_7 [\text{PCA}]_0$ . We can therefore recast (9) as

$$D_{457} = \frac{(\varepsilon_1 + \varepsilon_2 K_7 [\text{PCA}]_0) [\text{V}]_0}{1 + K_7 [\text{PCA}]_0} \left\{ 1 - \frac{[\text{H}_2\text{O}_2]_0}{K_6 (1 + K_7 [\text{PCA}]_0)} \right\}. \quad (10)$$

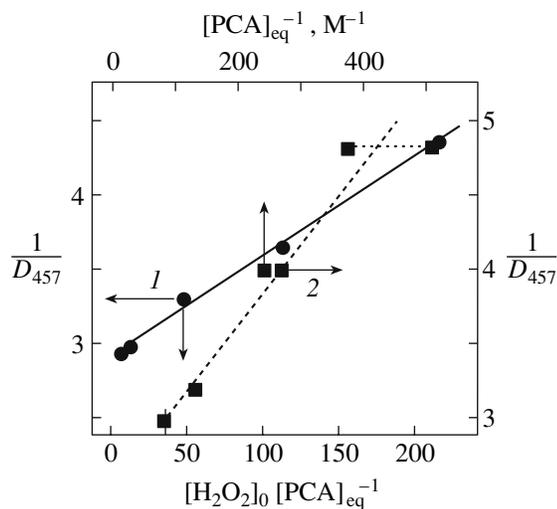
In agreement with (10), the experimental dependences at  $[\text{H}_2\text{O}_2]_0 > 0.01$  M (Fig. 2, curves 1 and 2) are linear. The y-intercept is

$$\alpha = \frac{(\varepsilon_1 + \varepsilon_2 K_7 [\text{PCA}]_0) [\text{V}]_0}{1 + K_7 [\text{PCA}]_0}, \quad (11)$$

and the ratio between the slope of the straight line and the segment is

$$\beta = 1/K_6 (1 + K_7 [\text{PCA}]_0). \quad (12)$$

It follows from these data that the  $\alpha$  value is virtually independent of the concentration of  $[\text{PCA}]_0$ . This is possible if (1) absorption in the electronic spectra is caused by the  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})$  particle whose concentration is the highest among all peroxo particles, and  $\alpha = \varepsilon_1 [\text{V}]_0$ ; (2) absorption is caused by the  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})_2$  complex whose concentration is the highest among peroxo particles, and  $\alpha = \varepsilon_2 [\text{V}]_0$ ; (3) the absorption coefficients of the complexes containing one and two PCA molecules are equal, that is,  $\varepsilon_1 = \varepsilon_2$  and  $\alpha = \varepsilon_1 [\text{V}]_0$ . The third variant is questionable. Because the experimental  $\beta$  parameter values are inversely proportional to the



**Fig. 3.** Dependences of  $1/D_{457}$  on the parameters (1)  $[H_2O_2]_0/[PCA]_{eq}$  and (2)  $[PCA]_{eq}^{-1}$  of solutions of  $n\text{-Bu}_4\text{NVO}_3$  (1 mM), PCA, and water (2.2 M) in isopropanol at  $50^\circ\text{C}$ ; (1)  $[PCA]_0 = 0.004$  M and (2)  $[H_2O_2]_0 = 0.5$  M.

concentration of PCA (for instance, for  $[PCA]_0 = 0.01$  and  $0.024$  M,  $\beta = 0.28$  and  $0.11$ , respectively), we have  $K_7[PCA]_0 > 1$  in (12), that is, vanadium monoperoxo complex containing two PCA molecules in the coordination sphere predominates ( $\beta \approx 1/K_6K_7[PCA]_0$ ). Using the  $\alpha$  and  $\beta$  values for curves 2 and 3 in Fig. 2, we obtain  $\varepsilon_2 = 320\text{--}360$   $\text{M}^{-1}\text{cm}^{-1}$  and  $K_6K_7 = 380\text{--}430$ .

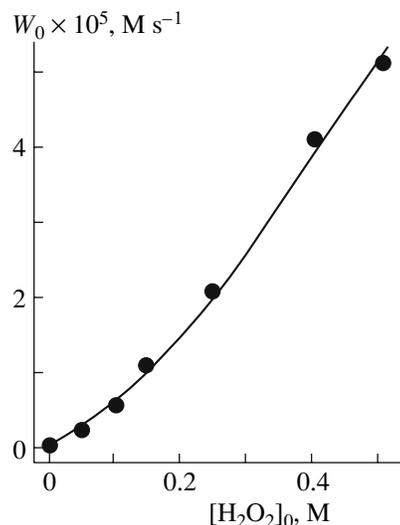
We found that (9) also described the experimental data obtained at  $[PCA]_0 = 0.004$  M if the equilibrium concentration  $[PCA]_{eq}$  was used instead of the concentration of PCA introduced into the solution (Fig. 2, curve 3 at  $[H_2O_2]_0 > 0.01$  M). A satisfactory linear dependence is then observed in the coordinates  $1/D_{457}$  versus  $[H_2O_2]_0/[PCA]_{eq}$  (Fig. 3), where  $[PCA]_{eq}$  is the equilibrium concentration of PCA not bound to a complex with vanadium. Under these conditions, the  $V(H_2O_2)(PCA)_2$  and  $V(H_2O_2)_2(PCA)$  particles predominate, and the equilibrium concentration of free PCA can therefore be written as

$$[PCA]_{eq} = [PCA]_0 - [V]_0 - [V(H_2O_2)(PCA)_2]. \quad (13)$$

The  $\varepsilon_2 = 340$   $\text{M}^{-1}\text{cm}^{-1}$  and  $K_6K_7 = 430$  values obtained from the dependence shown in Fig. 3 are close to those cited above.

Equation (9) can also be used to analyze the dependence of  $D_{457}$  on  $[PCA]_0$  close to the optical density maximum. We assume that only  $V(H_2O_2)(PCA)_2$  absorbs. Using this assumption, let us reduce (9) to a form that can conveniently be used to analyze the experimental data,

$$\frac{1}{D_{457}} = \frac{1}{\varepsilon_2[V]_0} + \frac{K_6 + [H_2O_2]_0}{\varepsilon_2[V]_0K_6K_7} \frac{1}{[PCA]_0}. \quad (14)$$



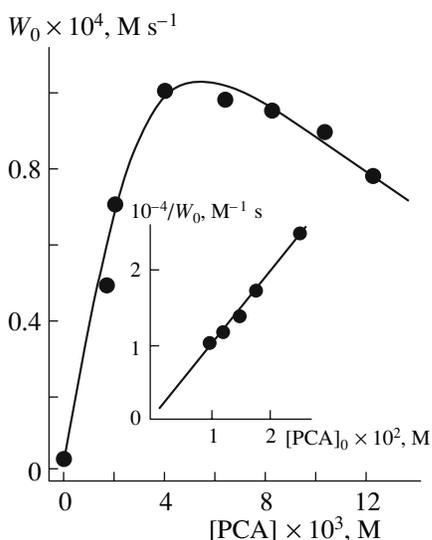
**Fig. 4.** Dependence of the initial rate of acetone accumulation  $W_0$  in the oxidation of isopropanol on the initial concentration of  $H_2O_2$  at  $[n\text{-Bu}_4\text{NVO}_3]_0 = 1$  mM,  $[PCA]_0 = 24$  mM,  $[(CH_3)_2CH(OH)]_0 = 12.4$  M,  $[H_2O] = 2.16\text{--}2.26$  M, and  $50^\circ\text{C}$ .

Although (9) is strictly valid only if  $[PCA]_0/[V]_0 \geq 10$ , it can be used at lower PCA concentrations if the equilibrium free acid concentration  $[PCA]_{eq}$  is substituted for  $[PCA]_0$  (see above). The validity of such an approach is substantiated by the results obtained in analyzing the dependence of  $D_{457}$  on  $[H_2O_2]_0$  in the region of high hydrogen peroxide concentrations ( $[H_2O_2]_0 \geq 0.01$  M), where the  $D_{457}$  value decreases at  $[PCA]_0 = 0.004$  M. Over the range of PCA concentrations  $0.004\text{--}0.015$  M that we are considering,  $D_{457}$  changes from 65 to 100% of its maximum value at  $[H_2O_2]_0 = 0.5$  M, and we can approximately assume that the equilibrium concentration of PCA in (14) can be written as

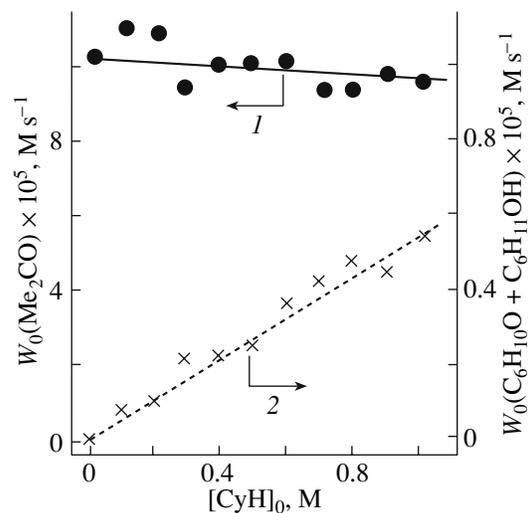
$$[PCA]_0 - 2[V(H_2O_2)(PCA)_2] \leq [PCA]_{eq} \leq [PCA]_0 - 2[V]_0. \quad (15)$$

The accuracy of such an analysis of the experimental data is not high. This analysis is, however, of interest, because it allows us to approximately estimate several other parameters of scheme (1)–(7). The linear dependence of  $1/D_{457}$  on  $1/[PCA]_{eq}$  (Fig. 3) corresponds to the transition of  $V(H_2O_2)(PCA)$  into  $V(H_2O_2)(PCA)_2$ , which absorbs light at 457 nm. The results presented in Fig. 3 allow us to obtain the estimates  $\varepsilon_2[V]_0 = 0.4$   $\text{cm}^{-1}$  ( $\varepsilon_2 = 400$   $\text{M}^{-1}\text{cm}^{-1}$ ) and  $(K_6 + [H_2O_2]_0)/K_6K_7 = 2.5 \times 10^{-3}$  M. With  $K_6K_7 \approx 400$ , we find that  $K_6 \approx 0.45$  M and, therefore,  $K_7 \approx 900$   $\text{M}^{-1}$ .

The initial rate of isopropanol oxidation  $W_0$  is directly proportional to the concentration of vanadate ions. The order of the reaction in  $[H_2O_2]$  is also close to one (Fig. 4). An increase in the reaction rate as the concentration of hydrogen peroxide grows under the conditions when the concentration of vanadium monoper-

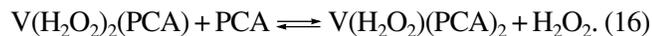


**Fig. 5.** Dependence of the initial rate of acetone accumulation  $W_0$  in the oxidation of isopropanol on the initial concentration of pyrazinecarboxylic acid at  $[n\text{-Bu}_4\text{NVO}_3]_0 = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ M}$ ,  $[(\text{CH}_3)_2\text{CH}(\text{OH})]_0 = 12.4 \text{ M}$ ,  $[\text{H}_2\text{O}] = 2.2 \text{ M}$ , and  $50^\circ\text{C}$ . The dependence of  $1/W_0$  on the initial concentration of pyrazinecarboxylic acid under the same conditions is shown in the inset.



**Fig. 6.** Dependences of the initial rates of (1) acetone and (2) cyclohexane oxidation product accumulation in the competing oxidation of isopropanol and cyclohexane in isopropanol on the initial concentration of cyclohexane at  $[n\text{-Bu}_4\text{NVO}_3]_0 = 1 \text{ mM}$ ,  $[\text{PCA}]_0 = 4 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ M}$ ,  $[\text{H}_2\text{O}] = 2.2 \text{ M}$ , and  $50^\circ\text{C}$ .

oxo complexes remains virtually unchanged shows that the rate-determining stage of the process is in all probability the monomolecular transformation of vanadium diperoxo complex containing one PCA molecule in the coordination sphere. A decrease in the reaction rate  $W_0$  as  $[\text{PCA}]_0$  increases (Fig. 5) is caused by the transformation



We assume that the rate-determining stage of isopropanol oxidation is the monomolecular transformation of the  $\text{V}(\text{H}_2\text{O}_2)_2(\text{PCA})$  complex. It is then easy to obtain the equation for the rate of the reaction at  $[\text{H}_2\text{O}_2]_0/[\text{V}]_0 \geq 10$  and  $[\text{PCA}]_0/[\text{V}]_0 \geq 10$ . Under these conditions, vanadium is present only in the form of peroxo complexes that either do or do not contain PCA in the coordination sphere. We therefore obtain

$$\begin{aligned} W &= k[\text{V}(\text{H}_2\text{O}_2)_2(\text{PCA})] \\ &= kK_4K_5[\text{V}]_0[\text{H}_2\text{O}_2]_0[\text{PCA}]_0 / \{1 \\ &+ K_4K_5K_6[\text{PCA}]_0(1 + K_7[\text{PCA}]_0) \\ &+ K_4[\text{H}_2\text{O}_2]_0(1 + K_5[\text{PCA}]_0)\}. \end{aligned} \quad (17)$$

In the region where  $W_0$  decreases as  $[\text{PCA}]_0$  increases (Fig. 5), the  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})$  and  $\text{V}(\text{H}_2\text{O}_2)(\text{PCA})_2$  particles are predominantly present, and the concentration of diperoxo complexes is low. Equation (17) can therefore be simplified,

$$W = k[\text{V}]_0[\text{H}_2\text{O}_2]_0/K_6(1 + K_7[\text{PCA}]_0). \quad (18)$$

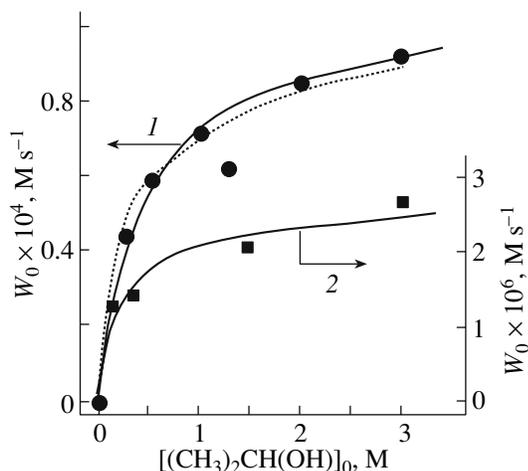
Experimental kinetic data processing according to (18) allows the  $K_6/k$  and  $K_7$  parameters to be determined. According to the data presented in Fig. 5, they equal  $0.065 \text{ M s}$  and  $700 \text{ M}^{-1}$ , respectively. The  $K_7$  values obtained from the spectrophotometric ( $900 \text{ M}^{-1}$ ) and kinetic ( $700 \text{ M}^{-1}$ ) measurements are close to each other. It follows that our concept of the mechanism of the reaction is in agreement with experiment. Using the  $K_6 = 0.45 \text{ M}$  value obtained above, we obtain the  $k \approx 7 \text{ s}^{-1}$  rate constant for the monomolecular decomposition of the  $\text{V}(\text{H}_2\text{O}_2)_2(\text{PCA})$  particle.

The oxidizing particle that appears in the vanadate ion–PCA– $\text{H}_2\text{O}_2$  catalytic system in isopropanol was identified by studying the competitive oxidation of three substrates (isopropanol, cyclohexane CyH, and acetonitrile) in isopropanol and acetonitrile. The data presented in Fig. 6 are evidence that there is competition between cyclohexane and isopropanol for the active intermediate particle X, whose appearance is controlled by the monomolecular transformation of vanadium diperoxo complex in isopropanol,



Let  $W_i$  denote the rate of X generation equal to the rate of isopropanol oxidation (that is, the rate of acetone formation) in the absence of cyclohexane. We can then write

$$W_i = \{k_{19}[\text{Me}_2\text{CH-OH}] + k_{20}[\text{CyH}]\}[\text{X}]. \quad (21)$$



**Fig. 7.** Dependences of the initial rate of acetone accumulation  $W_0$  in the oxidation of isopropanol in acetonitrile on the initial concentration of isopropanol at  $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ M}$  and  $[\text{H}_2\text{O}] = 2.2 \text{ M}$ ; (1) without irradiation and (2) under UV irradiation ( $\lambda \geq 253.0 \text{ nm}$ ); (1) 50 and (2) 20°C;  $[\text{nBu}_4\text{NVO}_3]_0 = (1) 1 \text{ mM}$  and (2) 0;  $[\text{PCA}]_0 = (1) 4 \text{ mM}$  and (2) 0; calculation results are shown by the dashed line.

According to (21), the sum of the rates of acetone and cyclohexylhydroperoxide CyOOH formation remains constant at various cyclohexane concentrations, which follows from Fig. 6. Using (21), we obtain

$$\frac{d[\text{CyOOH}]}{dt} = W_i \left/ \left( 1 + \frac{k_{19}[\text{Me}_2\text{CHOH}]}{k_{20}[\text{CyH}]} \right) \right. \quad (22)$$

As the rate of cyclohexane oxidation under all the conditions studied is much lower than the rate of isopropanol oxidation, we have

$$\frac{d[\text{CyH}]}{dt} = \frac{d[\text{CyOOH}]}{dt} = \frac{k_{20}[\text{CyH}]}{k_{19}[\text{Me}_2\text{CHOH}]} W_i \quad (23)$$

It follows from Fig. 6 that  $W_i = 10^{-4} \text{ M s}^{-1}$ , and the slope of the dependence of  $d[\text{CyOOH}]/dt$  on  $[\text{CyH}]$  is  $5 \times 10^{-6} \text{ s}^{-1}$ . Substituting  $[\text{Me}_2\text{CH-OH}]_0 = 12 \text{ M}$  into (23) yields  $k_{20}/k_{19} = 0.6$ . This means that the reactivities of cyclohexane and isopropanol with respect to particle X are similar.

On the other hand, the observed dependence of the rate of acetone formation on the concentration of added isopropanol in acetonitrile (Fig. 7) is evidence of a competition of isopropanol and acetonitrile for the intermediate oxidizing particle that appears in the catalytic system in acetonitrile. This competition is similar to that observed in the oxidation of cyclohexane in acetonitrile [13, 14]. The low parameters of bond selectivities in the oxidation of alkanes in acetonitrile and close ratios between the rate constants for the interaction of acetonitrile and cyclohexane with the intermediate particle formed in catalysis with vanadium (0.0083 [13, 14]) and photolysis of  $\text{H}_2\text{O}_2$  (0.013 [27, 28]) led us to conclude that the oxidizing particle in the catalytic sys-

tem in acetonitrile was the hydroxyl radical [13, 14]. An analysis of the data presented in Fig. 7 allowed us to determine the ratio between the rate constants for the interaction of hydroxyl radicals with acetonitrile and isopropanol, which was found to be 0.012. The dependence of the rate of acetone accumulation on  $[\text{Me}_2\text{CH-OH}]_0$  calculated using this ratio is shown in Fig. 7 by a dashed line. We see that the calculation results are in satisfactory agreement with the experimental data.

Figure 7 also contains the results of photochemical experiments performed to study the dependence of the rate of acetone formation on  $[\text{Me}_2\text{CH-OH}]_0$  in acetonitrile when hydrogen peroxide was subjected to photolysis in air. This dependence also corresponds to the competition between acetonitrile and isopropanol for the hydroxyl radical. The ratio between the rate constants of these reactions was estimated at  $k(\text{HO}^\bullet + \text{CH}_3\text{CN})/k(\text{HO}^\bullet + \text{Me}_2\text{CH-OH}) = 0.008$ . It follows that, in this case too, the ratios between the rate constants in different systems are in satisfactory agreement. The data obtained also show that the reactivities of cyclohexane and isopropanol with respect to the hydroxyl radical are close. This leads us to suggest that, as in acetonitrile, the oxidizing particle in isopropanol is the hydroxyl radical.

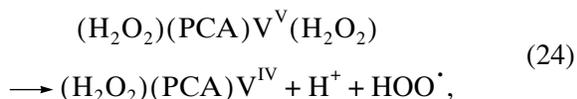
Note that the results of independent measurements of the rate constants for the interaction of hydroxyl radicals with acetonitrile, isopropanol, and cyclohexane can be found in the literature, but the spread of the values obtained is fairly wide. For instance, for the oxidation of acetonitrile, the  $3.6 \times 10^6$  and  $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  values were reported [29], and the values for cyclohexane and isopropanol were  $1.26 \times 10^9$  and  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [30, 31] and  $(1.7\text{--}2.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [32], respectively. The smallest spread of rate constants was obtained for isopropanol. We can therefore assume that  $k(\text{HO}^\bullet + \text{Me}_2\text{CH-OH}) = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This and the measurement results presented above allow us to calculate the rate constants  $k(\text{HO}^\bullet + \text{CH}_3\text{CN}) = (1.5\text{--}2.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{HO}^\bullet + \text{CyH}) = (1.1\text{--}1.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The vanadate ion-PCA- $\text{H}_2\text{O}_2$ -isopropanol and vanadate ion-PCA- $\text{H}_2\text{O}_2$ -acetonitrile catalytic systems are similar not only because the particle that oxidizes the substrate is the hydroxyl radical in both of them, but also because they are characterized by similar dependences of the rate of substrate oxidation on the initial concentration of hydrogen peroxide (compare Figs. 4 and 8). At a low  $\text{H}_2\text{O}_2$  concentration, the order of the reaction in  $[\text{H}_2\text{O}_2]_0$  is higher than first, but it is close to first at such  $\text{H}_2\text{O}_2$  concentrations at which the main fraction of vanadium is in the form of the monoperoxo complex according to the spectral data. An insignificant decrease in the order of the reaction in  $[\text{H}_2\text{O}_2]$  observed at high hydrogen peroxide concentrations correlates with a decrease in the fraction of vanadium present in the form of the monoperoxo complex detectable spec-

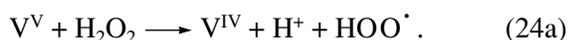
trophotometrically. The character of the dependence of the reaction rate on  $[\text{H}_2\text{O}_2]_0$  is consistent with the suggestion that vanadium diperoxo complex participates in the rate-determining reaction of hydroxyl radical generation.

We found that the rates of acetone formation in isopropanol and cyclohexane oxidation in acetonitrile have similar values under identical conditions (compare Figs. 6 and 7). Lastly, optical absorption at 457 nm was recorded in both systems under equal concentration conditions. This absorption relates to the monoperoxo complex containing the peroxy and PCA ligands in the coordination sphere. Changes in  $D_{457}$  follow the same pattern in isopropanol and acetonitrile. These data are evidence of identical mechanisms of oxidizing particle generation in both solvents. They also show that equilibrium constants of peroxy complex formation and the rate constants for the rate determining stage of diperoxo complex decomposition are closely similar. The new data obtained in this work for the formation and changes in the concentration of vanadium peroxy complexes in acetonitrile lead us to modify our earlier conclusions [13, 14] somewhat.

To summarize, the oxidation of isopropanol in isopropanol and alkanes in acetonitrile develops following similar schemes. The rate-determining stage of the process is likely the monomolecular decomposition of vanadium(V) diperoxo complex containing one PCA molecule in the coordination sphere. This decomposition is accompanied by electron transfer from the peroxide ligand to the V(V) ion and the formation of the peroxy radical and a vanadium(IV) derivative,

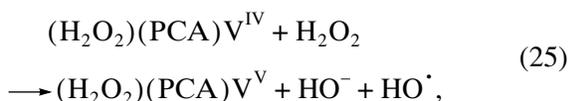


or, in a simpler form,



In [13, 14], the decomposition of the vanadium(V) monoperoxo complex was described by this scheme. The results obtained in this work, however, lead us to suggest that the diperoxo complex decomposes according to (24).

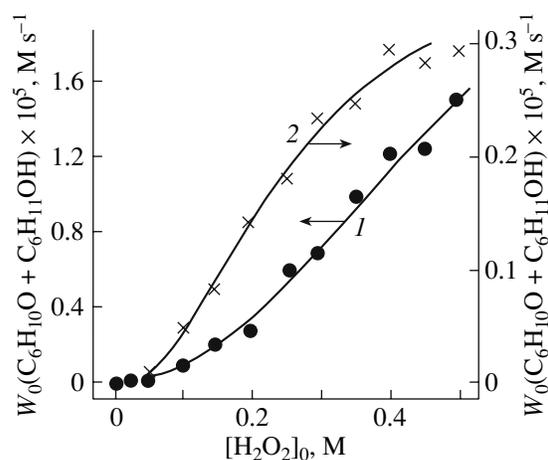
The interaction of the vanadium(IV) derivative with a new hydrogen peroxide molecule (possibly with the formation of a new diperoxo complex) results in the generation of the hydroxyl radical,



or, in a simpler form,

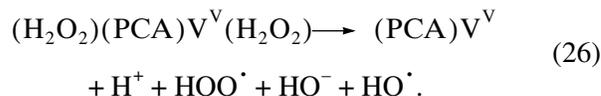


A somewhat different mechanism of the generation of radicals can be considered, when the vanadium diperoxo complex decomposes with the simultaneous participation of both peroxide ligands. One diperoxo complex molecule then generates both the peroxy and hydroxyl radicals either simultaneously or in two stages,



**Fig. 8.** Dependences of the initial rate of the accumulation of cyclohexane oxygenation products in the oxidation of cyclohexane in a solution in acetonitrile on the initial concentration of hydrogen peroxide at  $[\text{H}_2\text{O}] = 2.2 \text{ M}$  and  $40^\circ\text{C}$ ;  $[\text{n-Bu}_4\text{NVO}_3]_0 = (1) 0.5$  and  $(2) 0.1 \text{ mM}$ ,  $[\text{PCA}]_0 = (1) 2$  and  $(2) 0.4 \text{ mM}$ ,  $[\text{MeCN}]_0 = (1) 17.2$  and  $(2) 17.7 \text{ M}$ , and  $[\text{CyH}]_0 = (1) 0.46$  and  $(2) 0.20 \text{ M}$ .

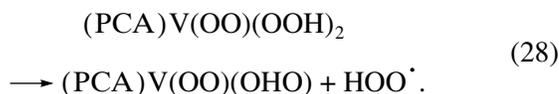
oxo complex decomposes with the simultaneous participation of both peroxide ligands. One diperoxo complex molecule then generates both the peroxy and hydroxyl radicals either simultaneously or in two stages,



The conclusion that it is the diperoxo complex that decomposes is also favored by the calculation results obtained in [19]. According to [19], the formation of the  $\text{HOO}^{\cdot}$  radical cannot occur as the rupture of the V–OOH bond in the complex formed in its simplest form directly from precursors, because the activation barrier to this process is too high. It was, however, found that  $\text{HOO}^{\cdot}$  radicals could form in several sequential stages characterized by lower activation barriers. It is noteworthy that, according to [19], the decomposition of the  $(\text{PCA})\text{V}(\text{OH})(\text{OO})(\text{OOH})$  complex (structure **12** in [19], that is, the diperoxo complex) with the participation of one acetonitrile molecule (reaction (11) in [19]),



and the  $(\text{PCA})\text{V}(\text{OO})(\text{OOH})_2$  complex (structure **17** in [19], in which the OO fragment is a monodentate ligand) without the participation of acetonitrile (reaction (17) in [19]),



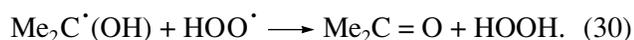
are the processes most favorable energetically.

The rate-determining reaction is the monomolecular decomposition of the vanadium diperoxo complex. In reality, this decomposition of  $V(H_2O_2)_2(PCA)$  accompanied by the generation of active particles can occur in a sequence of stages. One of these is hydrogen transfer from a coordinated hydrogen peroxide molecule to the vanadium oxo group. According to our suggestion of the role played by PCA in the process [13, 14] and the calculation results [19], this is the stage that determines the rate of the monomolecular decomposition of  $V(H_2O_2)_2(PCA)$ . The vanadium derivatives formed at this stage react with new hydrogen peroxide molecules and transform into active diperoxo complexes.

In the reaction with isopropanol, the hydroxyl radical abstracts a hydrogen atom,

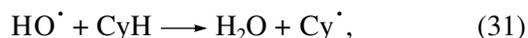


and the radical formed from isopropanol can (at least according to the formal scheme) react with the peroxy radical formed in reaction (24) or (26) to yield the oxidation product (acetone) and the hydrogen peroxide molecule,



This closes the catalytic cycle. Clearly, if the oxidation of isopropanol occurs in the absence of air oxygen, one hydrogen peroxide molecule is required to produce one acetone molecule.

The oxidation of the alkane (cyclohexane CyH) ends somewhat differently. The hydroxyl radical detaches a hydrogen atom from cyclohexane,



and the alkyl radical rapidly reacts with the oxygen molecule,



Formally, we can write the reaction



to close the catalytic cycle. This reaction yields the product (cyclohexylhydroperoxide). Clearly, the oxidation of alkanes requires two hydrogen peroxide molecules per one hydrocarbon molecule [14]. According to scheme (31)–(33), the second stage then proceeds with the consumption of an oxygen molecule, whereas, in reaction (33) (which was fairly formally introduced into the cycle), this molecule is released in the free form.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. G. B. Shul'pin, D. Attanasio, and L. Suber, *J. Catal.* **142**, 147 (1993).
2. G. B. Shul'pin and G. Süß-Fink, *J. Chem. Soc., Perkin Trans. 2*, p. 1459 (1995).
3. G. B. Shul'pin, R. S. Drago, and M. Gonzalez, *Izv. Akad. Nauk, Ser. Khim.*, p. 2514 (1996) [*Russ. Chem. Bull.* **45**, 2386 (1996)].
4. G. B. Shul'pin, M. C. Guerreiro, and U. Schuchardt, *Tetrahedron* **52**, 13051 (1996).
5. M. C. Guerreiro, U. Schuchardt, and G. B. Shul'pin, *Izv. Akad. Nauk, Ser. Khim.*, p. 780 (1997) [*Russ. Chem. Bull.* **46**, 749 (1997)].
6. A. E. Shilov and G. B. Shul'pin, *Chem. Rev.* **97**, 2879 (1997).
7. G. V. Nizova, G. Süß-Fink, and G. B. Shul'pin, *Tetrahedron* **53**, 3603 (1997).
8. U. Schuchardt, M. C. Guerreiro, and G. B. Shul'pin, *Izv. Akad. Nauk, Ser. Khim.*, p. 253 (1998) [*Russ. Chem. Bull.* **47**, 247 (1998)].
9. G. Süß-Fink, G. V. Nizova, S. Stanislas, and G. B. Shul'pin, *J. Mol. Catal. A: Chem.* **130**, 163 (1998).
10. G. B. Shul'pin, Y. Ishii, S. Sakaguchi, and T. Iwahama, *Izv. Akad. Nauk, Ser. Khim.*, p. 896 (1999) [*Russ. Chem. Bull.* **48**, 887 (1999)].
11. G. Süß-Fink, S. Stanislas, G. B. Shul'pin, et al., *J. Chem. Soc., Dalton Trans.*, p. 3169 (1999).
12. A. Shilov and G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes* (Kluwer, Dordrecht, 2000).
13. Yu. N. Kozlov, G. V. Nizova, and G. B. Shul'pin, *Zh. Fiz. Khim.* **75**, 865 (2001) [*Russ. J. Phys. Chem.* **75**, 770 (2001)].
14. G. B. Shul'pin, Y. N. Kozlov, G. V. Nizova, et al., *J. Chem. Soc., Perkin Trans. 2*, p. 1351 (2001).
15. G. B. Shul'pin, *J. Mol. Catal. A: Chem.* **189**, 39 (2002).
16. M. H. C. de la Cruz, Y. N. Kozlov, E. R. Lachter, and G. B. Shul'pin, *New J. Chem.* **27**, 634 (2003).
17. G. B. Shul'pin, *C. R. Acad. Sci., Ser. II: Chim.* **6**, 163 (2003).
18. Y. N. Kozlov, G. V. Nizova, and G. B. Shul'pin, *J. Mol. Catal. A: Chem.* **227**, 247 (2005).
19. R. Z. Khaliullin, A. T. Bell, and M. Head-Gordon, *J. Phys. Chem. B* **109**, 17984 (2005).
20. A. Butler, M. J. Clague, and G. E. Meister, *Chem. Rev.* **94**, 625 (1994).
21. E. P. Talsi and K. V. Shalyaev, *J. Mol. Catal.* **92**, 245 (1994).
22. V. Conte, F. Di Furia, and G. Licini, *Appl. Catal., A* **157**, 335 (1997).
23. M. Bonchio, O. Bortolini, M. Carraro, et al., *J. Inorg. Biochem.* **80**, 191 (2000).
24. M. Bonchio, O. Bortolini, V. Conte, and S. Primon, *J. Chem. Soc., Perkin Trans. 2*, p. 763 (2001).
25. C. Li, P. Zheng, J. Li, et al., *Angew. Chem., Int. Ed. Engl.* **42**, 5063 (2003).
26. M. Sam, J. H. Hwang, G. Chanfreau, and M. M. Abu-Omar, *Inorg. Chem.* **43**, 8447 (2004).

27. Yu. N. Kozlov, L. Gonzalez-Cuervo, G. Süss-Fink, and G. B. Shul'pin, *Zh. Fiz. Khim.* **77**, 652 (2003) [*Russ. J. Phys. Chem.* **77**, 575 (2003)].
28. G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, et al., *Adv. Synth. Catal.* **346**, 317 (2004).
29. Farhataziz and A. B. Ross, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions* (National Bureau of Standards, Washington, D.C., 1977), No. NSRDS-NBS 59.
30. E. S. Rudakov, L. K. Volkova, and V. P. Tret'yakov, *Soobshch. Kinet. Katal.* **16**, 333 (1981).
31. T. V. Khar'kova, I. L. Arest-Yakubovich, and V. V. Lipes, *Kinet. Katal.* **30**, 954 (1989).
32. L. M. Dorfman and G. E. Adams, *Reactivity of the Hydroxyl Radical in Aqueous Solutions* (National Bureau of Standards, Washington, D.C., 1973), NSRDS-NBS 46, p. 24.