Oxidations by the reagent "O_2–H_2O_2–vanadium derivative–pyrazine-2-carboxylic acid". Part 13.† Kinetics and mechanism of the benzene hydroxylation

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It has been concluded on the basis of the kinetic study of benzene hydroxylation by the "O_2–H_2O_2–$n\mathrm{Bu}_4\mathrm{NVO}_3$–PCA" reagent in acetonitrile at various temperatures that the oxidation is induced by the attack of hydroxyl radical on the benzene molecule. The rate-limiting step of the reaction is the monomolecular decomposition of the complex containing one coordinated PCA molecule as well as one hydrogen peroxide molecule: $\mathrm{V^{V}(PCA)(H_2O_2)} \rightarrow \mathrm{V^{IV}(PCA)} + \mathrm{HOO^{\bullet}} + \mathrm{H^{+}}$. The V(IV) species thus formed reacts further in a non-limiting stage with the second H_2O_2 molecule to generate the hydroxyl radical: $\mathrm{V^{IV}(PCA)} + \mathrm{H_2O_2} \rightarrow \mathrm{V^{V}(PCA)} + \mathrm{HO^{\bullet}} + \mathrm{HO^{-}}$. The effective activation energy is 19 ± 3 kcal mol^{-1}.

Introduction

Vanadium complexes are used in catalysis of many organic reactions[1,2] and they play very important roles in living organisms.[2,3] For example, vanadium can mimic some of insulin's actions, its complexes have been proposed as anti-tumor and anti-leukemic agents, V(IV) derivatives cause cessation of sperm motility. Some enzymes containing vanadium ions are capable of oxidizing C–H bond in organic compounds. Vanadium-containing haloperoxidases catalyse the halogenation of organic C–H compounds in the presence of hydrogen peroxide. Soluble vanadium compounds are also known as potent toxicants and carcinogens, which can act *via* generation of reactive oxygen species. Thus, hydroxyl radicals generated from molecular oxygen or hydrogen peroxide under the action of vanadium complexes in a living cell attack various cell components leading to their damage.

Earlier we have demonstrated that hydrogen peroxide oxidizes some organic substances, especially alkanes including very inert methane, in air, if a combination of tetrabutylammonium vanadate and pyrazine-2-carboxylic acid (PCA) is used as a catalyst.[4] Acetonitrile has been used as a solvent. At ambient temperature the reaction with alkanes gives rise predominantly to the formation of alkyl hydroperoxides whereas lower amounts of corresponding alcohols and ketones (aldehydes) are formed simultaneously. It was shown that atmospheric oxygen participates in this reaction, and when it is absent, no oxygenation occurs. This reagent gives a convenient method for efficient hydroperoxidation and oxygenation of alkanes under very mild conditions. The aim of the present work is to investigate the V-catalyzed hydrogen peroxide oxygenation of benzene.

It has been shown previously[4l,t] that the oxidative ability of the "O_2–H_2O_2–V complex–PCA" reagent in the reaction with cyclohexane is associated with the hydroxyl radical formation in the hydrogen peroxide decomposition. We have concluded on the basis of the kinetic investigation of the cyclohexane oxidation that the rate-limiting step of the reaction is the V(V) reduction in its monoperoxo complex containing one coordinated PCA molecule in the vanadium coordination sphere:

$$\mathrm{V^{V}(PCA)(H_2O_2)} \rightarrow \mathrm{V^{IV}(PCA)} + \mathrm{HOO^{\bullet}} + \mathrm{H^{+}}$$

The V(IV) oxidation by H_2O_2 in a non-rate-limiting stage of the process is accompanied by the formation of hydroxyl radicals:

$$\mathrm{V^{IV}(PCA)} + \mathrm{H_2O_2} \rightarrow \mathrm{V^{V}(PCA)} + \mathrm{HO^{\bullet}} + \mathrm{HO^{-}}$$

Experimental

Reactions were typically carried out in air in MeCN at 25 °C in thermostated Pyrex vessels with vigorous stirring. The total volume of the reaction solution was 5 mL. Initially, a portion of 46% aqueous solution of hydrogen peroxide was added to the solution of the catalyst, co-catalyst and benzene in acetonitrile (was distilled over P_2O_5 before the reaction).

Phenol in the samples of the reaction solutions was quantitatively determined by GC (instruments CG MASTER with fused silica capillary column 48 m × 0.25 mm × 0.25 µm, Carbowax 20 M, and Varian 3800 equipped with a capillary column VA-5, 30 m). Prior to the GC analysis the samples were treated with manganese oxide to decompose hydrogen peroxide. Special blank experiments demonstrated that no benzene hydroxylation occurs during this H_2O_2 decomposition.

Results and discussion

Hydroxyl radicals are known to be very strong oxidizing species and usually react extremely rapidly with organic compounds.[5] Therefore it is reasonable to expect the effective oxidation of various organic substances other than alkanes. It is, however, important to note that some organic compounds, unlike cyclohexane, are capable of forming complexes with vanadium ions which could affect the rate of hydroxyl radical formation and in some cases even change the reaction

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† For parts 1–12 see refs. 4(*a*)–(*l*), respectively.

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mechanism. In order to gain an additional mechanistic understanding of the oxidation reaction we studied the reaction with benzene which is known to interact effectively with hydroxyl radicals and, on the other hand, is potentially capable of coordinating to metal ions *via* its π-system.

Our experiments demonstrated that phenol is the main product in the benzene oxidation by the "O_2–H_2O_2–V complex–PCA" reagent, at least in the initial period of the reaction. Examples of kinetic curves of phenol accumulation in the course of the reaction are shown in Fig. 1. It follows from curves *3* and *4* that at temperatures > 35 °C the oxidation of benzene stops after 2 hours. In special experiments, we showed that if a relatively small amount of phenol is added to the reaction solution at the beginning of the reaction, the initial rate of benzene oxidation was lower and approximately equal to the rate determined at the moment when the same amount of phenol had been generated by benzene oxidation. Phenol is known to be able to coordinate metal ions, and addition of phenol to our reaction mixture decreased the benzene oxidation rate. This decrease of the benzene oxidation rate by relatively low concentrations of phenol may be also due to its reaction with hydroxyl radicals. In order to avoid the influence of formed phenol on the benzene oxidation rate we studied in the present work only the kinetics of the initial periods of the reaction, when the concentration of the formed phenol was relatively low and we could expect that the phenol effect on the rates was neglidgible.

Table 1 Oxidation of cyclohexane and benzene by the "O_2–H_2O_2–$n\mathrm{Bu_4NVO_3}$–PCA" reagent

Substrate/ mol dm^{-3}	$[\mathrm{PCA}]_0 \times 10^4$/ mol dm^{-3}	$[H_2O_2]_0$/ mol dm^{-3}	T/°C	$W \times 10^6$/ mol dm^{-3} s^{-1}
Cyclohexane				
0.46	4	0.24	20	0.5
0.46	4	0.24	50	12.5
Benzene				
0.90	5	0.30	20	0.7
0.90	5	0.30	50	10

In all cases $[n\mathrm{Bu_4NVO_3}] = 1 \times 10^{-4}$ mol dm^{-3}.

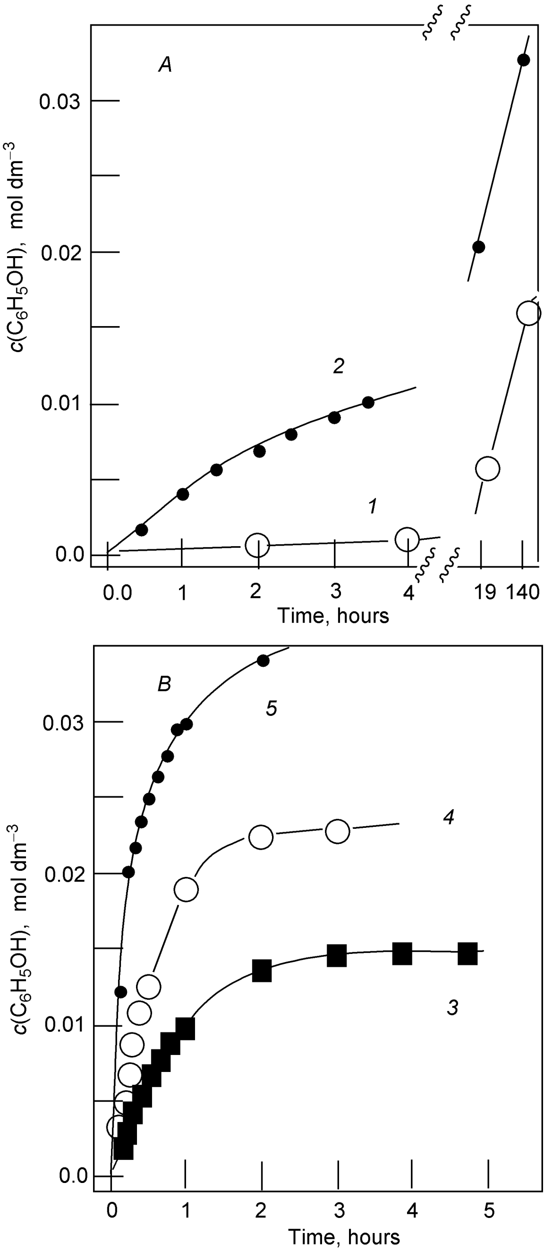

Fig. 1 Accumulation of phenol in the benzene oxidation. Conditions: $[n\mathrm{Bu_4NVO_3}] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{PCA}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2O_2]_0 = 0.30$ mol dm^{-3} (used as 46% aqueous solution), $[C_6H_6]_0 = 0.90$ mol dm^{-3}, 5 (curve *1*), 25 (curve *2*), 35 (curve *3*), 50 (curve *4*) and 60 °C (curve *5*).

Table 1 summarizes the results obtained for the benzene and (taken for comparison from ref. 4*l*) cyclohexane oxidation at high substrate concentrations [S], two different temperatures and similar concentrations of PCA and H_2O_2. It can be seen that the oxidation rates for both benzene and cyclohexane at the same temperatures practically coincide. On the basis of these data we can assume that, like cyclohexane, i) benzene does not affect the reactivity of the catalyst, and ii) the benzene oxidation rate is also limited by the hydroxyl-radical-formation rate. This assumption is supported by the coincidence of the activation energy rates for both cyclohexane and benzene oxidations. Indeed, in ref. 4*l* the efficient activation energy for the cyclohexane oxidation was found to be $E_a = 17 \pm 2$ kcal mol^{-1}, and its value for benzene oxidation (see Fig. 2) was $E_a = 19 \pm 3$ kcal mol^{-1}.

Since phenol is not produced in the absence of benzene, the data presented in Fig. 3 show that the reaction rate does not depend on $[\text{benzene}]_0$ at its relatively high concentrations (0.2 mol dm^{-3}), and this finding is in accordance with our assumption about the concurrence between the substrate (benzene) and the solvent (acetonitrile) in the interaction with the hydroxyl radical. Indeed, as the calculations demonstrate (see, for example, refs. 4*l*,*t*), at $[\text{benzene}]_0 \geqslant 0.2$ mol dm^{-3} more than 90% of formed hydroxyl radicals will react with benzene.

Dependences of the initial phenol formation rates, *W*(Phenol), on the concentration of added aqueous H_2O_2 solution

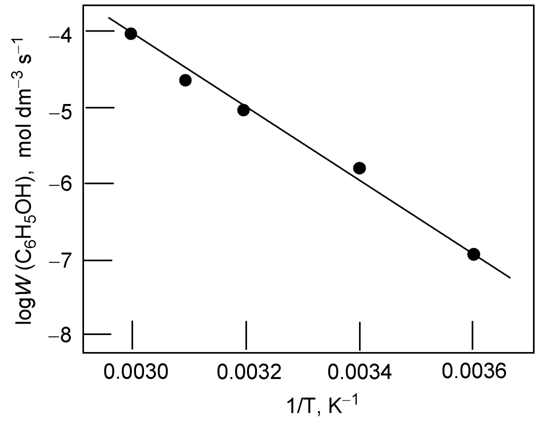

Fig. 2 Plot of logarithms of initial reaction rates *versus* inverse temperature. Conditions: $[n\mathrm{Bu_4NVO_3}] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{PCA}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2O_2]_0 = 0.30$ mol dm^{-3} (used as 46% aqueous solution), $[C_6H_6]_0 = 0.90$ mol dm^{-3}.

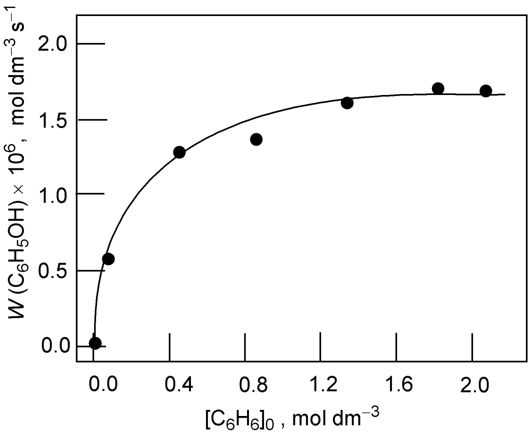

Fig. 3 Plot of the initial reaction rate *versus* initial benzene concentration. Conditions: $[n\text{Bu}_4\text{NVO}_3] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[\text{PCA}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}, $[\text{H}_2\text{O}_2]_0 = 0.60$ mol dm^{-3} (used as 46% aqueous solution), 25 °C.

and PCA at 25 °C are shown in Figs. 4 and 5*a*, respectively. These dependences are similar to those obtained earlier for cyclohexane oxidation at 40 °C.[4l,t] As in the experiments with cyclohexane,[4l,t] the benzene oxidation rate is directly proportional to both the full catalyst ($VO_3^- + \text{PCA}$) and vanadate concentrations (Fig. 6). The decrease in the benzene oxidation rate at high concentrations of added hydrogen peroxide is due to the influence of water introduced into the reaction solution with hydrogen peroxide. If we take into account this rate-decreasing effect of water, we come to the independence of *W*(Phenol) on the H_2O_2 concentration, and this independence corresponds to the transformation of all vanadium ions into the monoperoxo complex. Some quantitative difference between the parameters obtained in the present work for benzene oxidation and the data reported by us previously for cyclohexane oxidation has been found. This difference could be due to the temperature dependence of the constants of equilibrium intermediate complex formation as well as of the rate constants for the monomolecular decomposition of the reactive monoperoxo complex.

We analyzed the obtained dependence of the benzene oxidation rate on the PCA concentration in terms of the mechanism for hydroxyl radical generation.[4l,t] The following steps were proposed for this process:

$$\text{V} + \text{PCA} \rightleftarrows \text{V(PCA)} \quad K_1 \tag{1}$$

$$\text{V(PCA)} + \text{PCA} \rightleftarrows \text{V(PCA)}_2 \quad K_2 \tag{2}$$

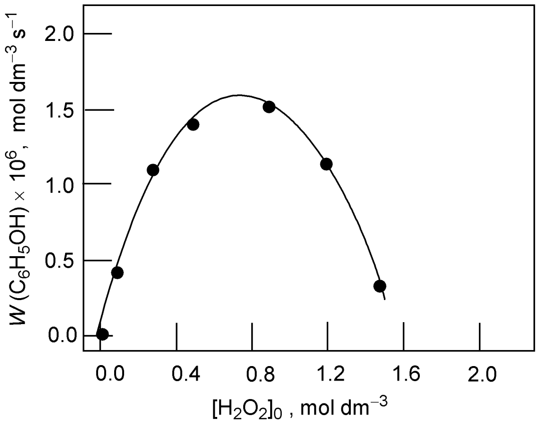

Fig. 4 Plot of the initial reaction rate *versus* initial H_2O_2 concentration. Conditions: $[n\text{Bu}_4\text{NVO}_3] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[\text{PCA}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}, $[C_6H_6]_0 = 0.90$ mol dm^{-3}, 25 °C.

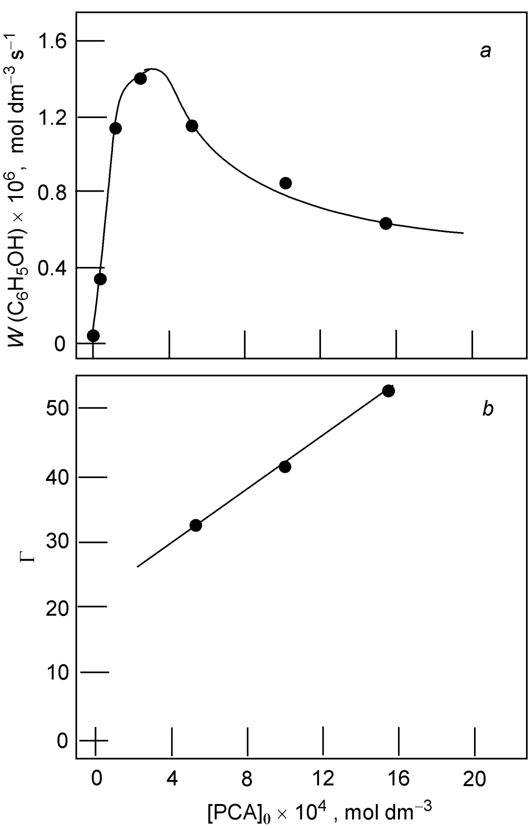

Fig. 5 Plot of the initial reaction rate *versus* PCA concentration (graph *a*) and its anamorphosis in coordinates Γ–$[\text{PCA}]_0$ (graph *b*). Conditions: $[n\text{Bu}_4\text{NVO}_3] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[C_6H_6]_0 = 0.90$ mol dm^{-3}, $[H_2O_2]_0 = 0.30$ mol dm^{-3} (used as 46% aqueous solution), 25 °C.

$$\text{V(PCA)} + \text{H}_2\text{O}_2 \rightleftarrows \text{V(PCA)(H}_2\text{O}_2) \quad K_3 \tag{3}$$

$$\text{V(PCA)(H}_2\text{O}_2) \rightleftarrows \text{V(H}_2\text{O}_2) + \text{PCA} \quad K_4 \tag{4}$$

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

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

$$\text{V}^{\text{V}}\text{(PCA)(H}_2\text{O}_2) \rightarrow \text{V}^{\text{IV}}\text{(PCA)} + \text{H}^+ + \text{HOO}^\bullet \quad k_7 \tag{7}$$

$$\text{V}^{\text{IV}}\text{(PCA)} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{\text{V}}\text{(PCA)} + \text{HO}^\bullet + \text{HO}^- \quad k_8 \tag{8}$$

Phenol is further formed in this process *via* a sequence of the stages which do not limit the oxidation rate:[6]

$$\text{C}_6\text{H}_6 + \text{HO}^\bullet \rightarrow \text{C}_6\text{H}_6\text{(OH)}^\bullet$$

$$\text{C}_6\text{H}_6\text{(OH)}^\bullet + \text{O}_2 \rightarrow \text{C}_6\text{H}_6\text{(OH)(OO)}^\bullet$$

$$\text{C}_6\text{H}_6\text{(OH)(OO)}^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HOO}^\bullet$$

Expression (9) for the steady reaction rate proposed in refs. 4*l*,*t* for the case when all hydroxyl radicals generated in the reaction mixture are accepted by the benzene is applicable only at concentrations of PCA higher than the concentration of the vanadium catalyst. Taking this into account we have analyzed the data shown in Fig. 5*a* only for the concentration $[\text{PCA}]_0 \geqslant 2.5 \times 10^{-4}$ mol dm^{-3}. In the kinetic study (eqn. 9) we use the initial concentration $[\text{PCA}]_0$, that is the total concentration of PCA introduced into the reaction solution. Usage of $[\text{PCA}]_0$ is reasonable only for the case when the decrease in the PCA concentration in the solution due to its binding to vanadium ion is not large. Since the concentration of PCA complexed with vanadium ion is not higher than $[\text{V}]_0$, it can be concluded that at $[\text{PCA}]_0/[\text{V}]_0 \geqslant 5$ the difference between the concentration of free PCA in the solution and the initial concentration $[\text{PCA}]_0$ is not more that 20%. This fact allows us to analyze the data presented in Fig. 5*b* using the

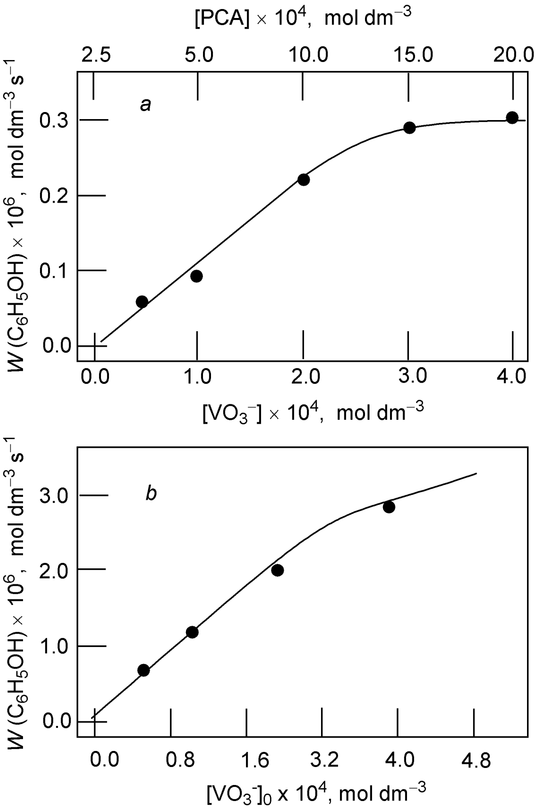

Fig. 6 Plot of initial reaction rate *versus* catalyst ($[VO_3^-] + 5[PCA]$) concentration (graph *a*) and plot of initial reaction rate *versus* initial VO_3^- concentration at fixed PCA (5.0×10^{-4} mol dm^{-3}) concentration (graph *b*). Conditions: $[H_2O_2]_0 = 0.3$ mol dm^{-3}, $[C_6H_6]_0 = 0.9$ mol dm^{-3}, 25 °C.

$[PCA]_0$ parameter in accordance with eqn. 9. However, at $[PCA]_0/[V]_0 < 5$, the fraction of PCA complexed with vanadium (that is concentration [PCA]) in comparison with initial $[PCA]_0$ can be substantial. In this case the approximation $[PCA] \approx [PCA]_0$ is not right and eqn. 9 is not applicable. In order to analyze the data under these conditions, it would be necessary to obtain an expression for the reaction rate taking into account the mass balance equation not only for vanadium but also for PCA. It is evident that unfortunately the rate equation will be extremely complex in this case.

$$W(\text{Phenol}) = \frac{d[C_6H_5OH]}{dt} = \frac{2k_7K_3[H_2O_2]_0[PCA]_0[V]_0}{K_2(1+K_5[H_2O_2]_0)[PCA]_0^2 + (1+K_3[H_2O_2]_0)[PCA]_0 + K_3K_4[H_2O_2]_0} \qquad (9)$$

Using the anamorphosis Γ of the W dependence on $[PCA]_0$ (see ref. 4*l*), expressed by eqn. 10, and eqn. 11 for $[PCA]_{max}$, we obtained the dependence $\Gamma = f([PCA]_0)$. Here $[PCA]_0$ is the initial PCA concentration and $[PCA]_{max}$ is the PCA concentration at which the maximum value is attained for the reaction rate at the fixed H_2O_2 concentration.

$$\begin{aligned}\Gamma &= \frac{[V]_0[H_2O_2]_0}{[PCA]_0 - [PCA]_{max}}\left\{\frac{[PCA]_0}{W} - \frac{[PCA]_{max}}{W_{max}}\right\}\\ &= \frac{1}{2k_7K_3} \times \{(1 + K_3[H_2O_2]_0)\\ &\quad + K_2(1 + K_5[H_2O_2]_0)([PCA]_0 + [PCA]_{max})\}\end{aligned} \qquad (10)$$

$$[PCA]_{max} = \sqrt{\frac{K_3K_4[H_2O_2]_0}{K_2(1 + K_5[H_2O_2]_0)}} \qquad (11)$$

It is clearly seen in Fig. 5*b* that the experimental data are in good agreement with the proposed kinetic equation. Based on these data we were able to calculate the following parameters: $K_3 = 1.8$ dm^3 mol^{-1}; $K_2K_5 = 6 \times 10^3$ dm^6 mol^{-2}; $K_4 = 5 \times 10^{-4}$ mol dm^{-3}. In these calculations we accepted the value for k_7K_3 obtained in ref. 4*l* at 40 °C and extrapolated to 25 °C taking $E_a = 17 \pm 2$ kcal mol^{-1}. Some increases in the values of equilibrium constants for the formation of species $V(PCA)(H_2O_2)$ from V(PCA) and H_2O_2 as well as of the product of constants K_2K_5 when the temperature declines can be assumed. These increases looks reasonable because usually enthalpies of formation of these types of complexes are negative. For the same reason the constant of equilibrium (4) decreases with increasing temperature.

Finally, using the data obtained in the present work as well as parameters from ref. 4*l*, we estimated the enthalpies of processes (3) and (4) as well as of the sum of processes (2) and (5), which equal −14, +35 and −23 kcal mol^{-1}, respectively. Using the values of K_3 at 25 and 40 °C and activation energy k_7K_3 we estimated also the activation energy of the monomolecular decomposition of peroxovanadium complex, $E_7 = 31 \pm 3$ kcal mol^{-1}.

It is interesting to compare the activities of the vanadium-based system described in this paper and the known iron-containing "Fe(III)–Fe(II)–H_2O_2" system. Let us consider the activities of the peroxyl complex $Fe^{III}(OOH)^{2+}$ (eqn. 12) and the analogous vanadium(V) peroxy derivative $V^V(PCA)(H_2O_2)$ (eqn. 7) in monomolecular decomposition reactions to generate active species

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HOO^{\bullet} \quad k = 1.6 \times 10^{-3} s^{-1} \qquad (12)$$

The constant for the vanadium complex is $k_7 = 0.4$ s^{-1} at 40 °C and the corresponding value for the iron compound is $k_{12} = 1.6 \times 10^{-3}$ s^{-1} at 25 °C. Using the value $E_{12} = 22$ kcal mol^{-1} we can estimate $k_{12} = 10^{-2}$ s^{-1} at 40 °C. It can be concluded that the activity of the vanadium complex with PCA in the generation of radicals in acetonitrile solution is more than one order of magnitude higher than that of Fe(III) ion in acidified aqueous solution.

Conclusions

Saturated and aromatic hydrocarbons differ dramatically in the mechanisms of their reactivity with radical species; for example, hydroxyl radicals abstract hydrogen atoms from alkanes to produce the corresponding alkyl radicals whereas benzene derivatives add to these radicals to afford species with electrons delocalized between a few ring carbon atoms. The kinetic study of benzene hydroxylation by the "O_2–H_2O_2–V complex–PCA" reagent, carried out in this work, demonstrated that the reagent oxidizes aromatic compounds with participation of hydroxyl radicals as crucial reactive species. Indeed, since the kinetic behaviour of the system under discussion is similar for both saturated and aromatic substrates we propose that the rate-limiting step of the process is the monomolecular decomposition of the vanadium(V) complex containing one coordinated PCA molecule, and this step does not depend on the nature of the substrate used. Both aliphatic alcohols and phenols are further formed in the stages which do not limit the oxidation rate. Like saturated cyclohexane, benzene does not affect the reactivity of the catalyst, and thus no strong complexation between the vanadium species and the benzene π-system can be assumed. Meantime, unlike aliphatic alcohols formed from alkanes, phenols decrease the benzene oxidation rate which may be due to the coordination of phenols with vanadium ion and/or to their reaction with hydroxyl radicals.

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