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Role of the $V^{(V)}/{}^1O_2$ Complex in Oxidative Reactions in the $H_2O_2/V^{(V)}/AcOH$ System: Oxidation of Alkenes and Anthracenes

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Abstract—Anthracene and its alkyl derivatives undergo oxidation in the $V^{(V)}/H_2O_2/AcOH$ system via a nonradical mechanism through the intermediate formation of the vanadium(V) complex with singlet dioxygen as a ligand. The ${}^1O_2$ molecule is transferred from this complex to an unsaturated substrate. The free singlet dioxygen ${}^1O_2({}^1\Delta_g)$ is almost inactive toward anthracene in AcOH solution. Consequently, the vanadium(V) complex with singlet dioxygen is the only oxidant species active in the reaction. The ratio between the rate constant of the reaction of this complex with 2-ethylanthracene and the rate constant of its deactivation is an order of magnitude greater than the ratio between the rate constant of the reaction of dissolved free singlet dioxygen with the same substrate and the rate constant of its deactivation (physical quenching).

INTRODUCTION

The hydroperoxide oxidation of aromatic hydrocarbons in the presence of transition metal compounds has been known since its discovery by Fenton [1]. The mechanism of operation of catalysts containing metal atoms that can readily take at least two oxidation states, for example, Fe(II)–Fe(III)–Fe(IV)–Fe(V), has been studied in detail [2]. The reactivity of hydroperoxides and their metal complexes is known to be sensitive to the nature of solvents, metal ions, and ligand surroundings [3–5]. In the case of complexes of metals with d^0 nonbonding configuration, molecular pathways of H_2O_2 activation are possible [6–11].

Hydrogen peroxide decomposition to form triplet dioxygen and water (reaction (I)) is thermodynamically favorable (Table 1). The reaction occurs in the presence of Fe, Co, Cu, and other catalysts:

$$2H_2O_2 \longrightarrow {}^3O_2 + 2H_2O. \qquad \text{(I)}$$

Compounds such as $Ca(OH)_2$, H_2TiO_3, $NaVO_3$, Na_2MoO_4, and Na_2WO_4 in an alkaline medium [12] and $V^{(V)}$ complexes in acetic acid [6–11, 13, 14] can catalyze H_2O_2 decomposition with the formation of singlet dioxygen (reaction (II)), although this reaction is thermodynamically less favorable than reaction (I) (Table 1)

$$2H_2O_2 \longrightarrow {}^1O_2 + 2H_2O. \qquad \text{(II)}$$

Ozone formation in the decomposition of H_2O_2 is thermodynamically consistent (Table 1). The catalytic hydrogen peroxide decomposition to form ozone (reaction (III)) was observed in the presence of vanadium compounds in CH_3COOH (~1% yield) and CF_3COOH (~10–13% yield) [7, 15]

$$3H_2O_2 \longrightarrow O_3 + 3H_2O. \qquad \text{(III)}$$

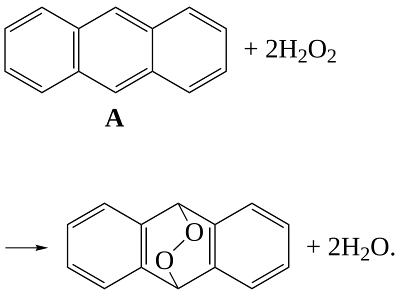
A number of $V^{(V)}$-catalyzed oxidation reactions with the participation of H_2O_2 catalyzed by $V^{(V)}$ complexes in carboxylic acid solutions have been studied [6–11, 13, 14]. It was concluded from these data that one-electron reduction of $V^{(V)}$ by H_2O_2 does not occur in these systems. In neutral or acidic aqueous solutions, the interaction of H_2O_2 with $V^{(V)}$ results in the formation of peroxo complexes like $[V(O_2)_nO_m]^{5-2(n+m)+}$, where m, n = 1, 2. These complexes are stable in aqueous solutions at ambient temperature [16, 17]. However, they can catalyze the decomposition of H_2O_2 and peracetic acid in an acetic acid solution [18]. In an AcOH medium, alkenes are selectively oxidized into the corresponding aldehydes [11], 2-ethylanthracene is oxidized into 2-ethylanthraquinone [13], and cyclohexane is oxidized into cyclohexanol and cyclohexanone [8].

Table 1. Free energy of H_2O_2 decomposition

Product of H_2O_2 decomposition	ΔG^0_{298}, kcal/mol
${}^3O_2$	–56
${}^1O_2$	–24
O_3	–45

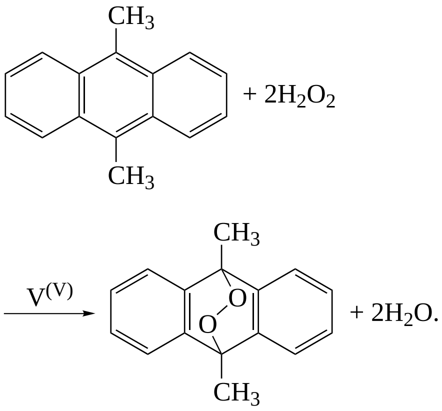
The previous data on anthracene oxidation suggest that singlet dioxygen is involved into the reaction. Thus, in the oxidation of anthracene (A) with H_2O_2 in AcOH in the presence of $V^{(V)}$, the yield of anthraquinone is as high as 100%. Anthrone, bianthrone, and the anthracene radical cation were not detected under conditions of anthracene oxidation in the $H_2O_2/V^{(V)}/AcOH$ system. These facts suggest that the reactive species cannot be responsible for one-electron oxidation of the substrate molecule.

According to the ^1H NMR and GC–MS data, 9,10-dihydro-9,10-epidioxyanthracene (**1**) is the primary product of anthracene oxidation under these conditions [10, 13]:



(IV)

endo-Peroxide **1** is unstable, and it rapidly transforms to the final reaction product, anthraquinone [19]. Direct experimental evidence for this mechanism was obtained in the oxidation of 9,10-dimethylanthracene in the $H_2O_2/V^{(V)}/AcOH$ system [7, 10, 11]:



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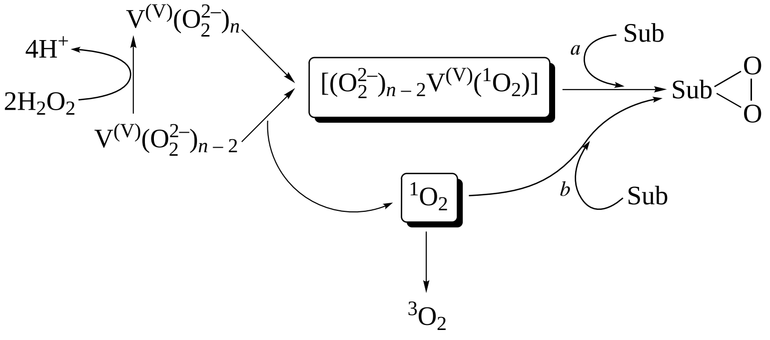
(V)

The yellow crystalline product formed in ~90% yield within 1 h at 20°C was characterized by elemental analysis, NMR spectroscopy, and GC–MS [11]. The ^1H and ^{13}C NMR spectra and the presence of the peroxo group in the reaction product (found by iodometry) indicate unambiguously that 9,10-dimethylanthracene was oxidized to 9,10-dimethyl-9,10-epidioxyanthracene (**2**) (reaction (V)). The formation of *endo*-peroxides upon the oxidation of anthracenes gives direct evidence for the involvement of singlet dioxygen into oxidation [20].

The formation of compounds **1** and **2** can be rationalized using a scheme that includes assuming the formation of an intermediate vanadium(V) complex with singlet dioxygen as a ligand. Both the interaction of this complex with a substrate molecule (Scheme 1, route *a*) and the reaction of the substrate with the dissolved free singlet dioxygen formed from this complex (Scheme 1, route *b*) can produce *endo*-peroxides.



Scheme 1. Possible routes of the oxidation of anthracenes (Sub) in the $H_2O_2/V^{(V)}/AcOH$ system.

The chemiluminescence spectrum of $^1O_2$ at 1275 nm [21–24] is indicative of the presence of free singlet dioxygen in the reaction solutions. The lifetime of $^1O_2$ in AcOH estimated from the kinetics of phosphorescence photosensitized by hematoporphyrin is 23 ± 1 μs [24]. Consequently, the maximal steady-state concentration of $^1O_2$ reached in the catalytic decomposition of H_2O_2 (1 mol/l) is no higher than ~3×10^{-9} mol/l.

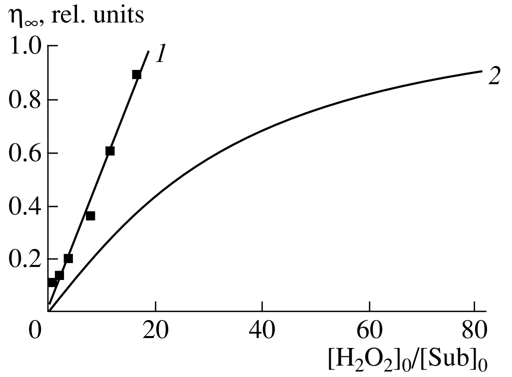


Fig. 1. Plots of the limiting 2-ethylanthracene conversion (η_∞) vs. the ratio $\frac{[H_2O_2]_0}{[Sub]_0}$: (*1*) experimental curve; $[Sub]_0 = 8.45 \times 10^{-3}$ mol/l; $[V] = 3.61 \times 10^{-3}$ mol/l; 30°C and (*2*) curve calculated under the assumption that free dissolved $^1O_2$ is the active oxidant (Eq. (2)).

Another species, which can be considered an active oxidant, is the complex $[(O_2^{2-})_{n-2}V^{(V)}(^1O_2)]$ (n = 2 or 3) containing $^1O_2$ as a ligand[1] (Scheme 1). To determine the contributions of routes *a* and *b* in Scheme 1, we studied the kinetics of oxidation of 2-ethylanthracene in the $H_2O_2/V^{(V)}$/AcOH system.

EXPERIMENTAL

Reagents and Materials

Acetic acid, toluene, benzene, hexadecane, decane, and an aqueous solution of hydrogen peroxide (9.67 mol/l) of chemically pure grade were used without additional purification. A concentrated solution of H_2O_2 (15 mol/l) was prepared by distilling commercial H_2O_2 (analytical grade). Anthracene, 9-methylanthracene, 9-phenylanthracene, 9,10-dimethylanthracene, 2-ethylanthracene, *trans*-1,2-diphenylethylene, 1,1-diphenylethylene (all of at least 95% purity according to GLC data), and NH_4VO_3 (analytical grade) were used without further purification. Commercial $VO(acac)_2$ was purified by recrystallization from $CHCl_3$. α-Methylstyrene (chemically pure grade) was distilled before use, and its purity was checked by GLC.

Preparation of the Catalyst Solution

To prepare a solution of $V^{(V)}$ in AcOH, finely ground NH_4VO_3 (100 mg) was refluxed in 100 ml of AcOH for 4 to 5 h. The undissolved NH_4VO_3 was filtered off. The concentration of $V^{(V)}$ in the resulting solution was 3.7×10^{-3} mol/l, as measured on an HP 4500 ICP–MS spectrometer (NH_4VO_3 as the external standard). In some kinetic runs, $VO(acac)_2$, whose solubility in AcOH is much higher, was used as the parent compound for catalysts. ESR spectra showed that the signal due to $V^{(IV)}$ from $VO(acac)_2$ disappeared after the first H_2O_2 drops were added to the reaction solution. When NH_4VO_3 was used instead of $VO(acac)_2$, the composition of the reaction products and the reaction rate remained unaffected.

Decomposition of H_2O_2

The reaction was studied at 30°C using a constant-temperature Pyrex reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 4.4 ml (42.5 mmol) of an aqueous solution of H_2O_2 (9.67 mol/l) was added to a solution of $VO(acac)_2$ (1.33 mg, 0.005 mmol) in 50 ml of AcOH. The withdrawn samples were diluted with 3-ml portions of an aqueous 1 M H_2SO_4 solution. The rate of H_2O_2 decomposition was followed by iodometric titration.

Oxidation of Substrates and Analysis of Reaction Products

The competitive oxidation of 1,1-diphenylethylene, *trans*-1,2-diphenylethylene, α-methylstyrene, anthracene, and its derivatives was carried out at 30°C in a thermostatted Pyrex reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 0.09 ml (1.6 mmol) of an aqueous 17.8 mol/l solution of H_2O_2 was added to a solution of 7.55 mg (0.0285 mmol) of $VO(acac)_2$, 17.8 mg (0.0989 mmol) of 1,1-diphenylethylene, 17.0 mg (0.0942 mmol) of *trans*-1,2-diphenylethylene, and 13.5 mg (0.0756 mmol) of anthracene in 10 ml of glacial acetic acid. The residual concentrations of the reactants were determined by GLC after the complete consumption of hydrogen peroxide (~2 h after mixing the reactants).

The ratio of the rate constant of a substrate reaction to that of an anthracene reaction (relative rate constant) was calculated by the equation [25]

$$\frac{k_i}{k_A} = \frac{\ln\frac{[Sub]}{[Sub]_0}}{\ln\frac{[A]}{[A]_0}}, \qquad (1)$$

where [Sub] and $[Sub]_0$ are the final and initial concentrations of the substrate Sub, respectively, and [A] and $[A]_0$ are the final and initial concentrations of anthracene, respectively. The oxidation of 2-ethylanthracene was studied at 30°C in a thermostatted Pyrex

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[1] The O_2 molecule is formed in the disproportionation of two O_2^{2-} ligands. Two O^{2-} ligands (protonated or unprotonated) should also be formed in this reaction. Because we have no reliable data on other ligands in the composition of this complex, ligands other than $^1O_2$ and O_2^{2-} are omitted.

reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, 0.0966 ml (1.72 mmol) of an aqueous 17.8 mol/l solution of H_2O_2 was added to a solution of $VO(acac)_2$ (2.10 mg, 7.93×10^{-3} mmol) and 2-ethylanthracene (58.5 mg, 0.284 mmol) in 14.2 ml of glacial acetic acid. The reaction solution was sampled using 0.5-ml samples after 2, 4, 6, 8, 12, and 25 min. The rate of H_2O_2 decomposition was followed by iodometric titration. The concentrations of the substrates were determined by GLC.

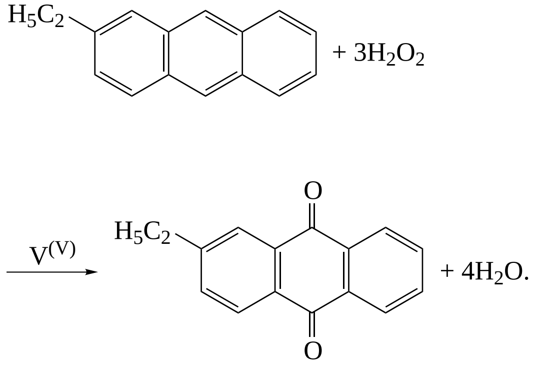
Analysis for diphenylethylenes and α-methylstyrene: a solution of dodecane (10^{-2} mol/l, GLC internal standard) in benzene (0.5 ml) was added to 0.5 ml of the reaction solution. The mixture was separated into layers after the addition of 5 ml of water. The organic layer was separated and washed with 1 ml of a 5% solution of sodium carbonate. The GLC analysis was carried out on a 3700 chromatograph (Russia) (HP-1 capillary column, 0.2 mm × 25 m, 0.33 μm; FID) using an ITs-26 integrator (Bulgaria). GLC conditions: $T_{injector} = 250°C$, $T_{column} = 120°C$, 2 min, programmed heating at a rate of 10°C/min up to 200°C, 2 min; $P = 1$ bar; split ratio of 1/40.

Sample preparation for the determination of anthracene, 2-ethylanthracene, 9-methylanthracene, 9,10-dimethylanthracene, and 9-phenylanthracene was carried out as described above using 0.5 ml of a 10^{-2} mol/l solution of hexadecane in benzene.

Conditions of GLC analysis: $T_{injector} = 270°C$, $T_{column} = 200°C$, 2 min, programmed heating at a rate of 10°C/min up to 270°C, 2 min; $P = 1$ bar; split ratio of 1/40.

RESULTS AND DISCUSSION

Under the conditions of the kinetic experiment, 2-ethylanthraquinone is the main product (60–90% yield) of 2-ethylanthracene oxidation in the $H_2O_2/V^{(V)}/AcOH$ system



(VI)

In the oxidation of 2-ethylanthracene, about 2–7% 2-acetylanthraquinone was detected in the reaction solution (this is the only detected by-product). 2-Ethylanthrone was not found when chromatographic and spectrochemical techniques were employed. Therefore, the chain-radical mechanism of 2-ethylanthracene oxidation can be excluded from consideration.

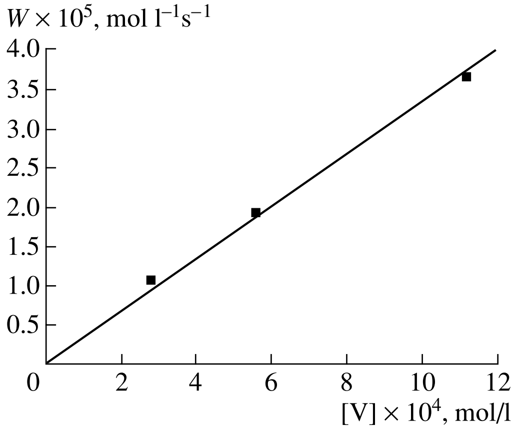


Fig. 2. Initial rate of 2-ethylanthracene oxidation as a function of catalyst concentration. $[Sub]_0 = 6.0 \times 10^{-3}$ mol/l; $[H_2O_2]_0 = 0.144$ mol/l; 34.5°C.

Under the assumption that ${}^1O_2({}^1\Delta_g)$ is an active oxidant species in the $H_2O_2/V^{(V)}/AcOH$ system (Scheme 1, route *b*) and the yield of ${}^1O_2$ in hydrogen peroxide decomposition is close to 100%, the consumption of 2-ethylanthracene and H_2O_2 can be described by the equation

$$\frac{d[H_2O_2]}{d[Sub]} = 2\frac{k_d + k_s[Sub]}{k_s[Sub]}, \qquad (2)$$

where [Sub] is the substrate (2-ethylanthracene) concentration, $k_d = 4.4 \times 10^4$ s^{-1} is the rate constant of ${}^1O_2$ quenching in AcOH, and $k_s = 3 \times 10^5$ mol l^{-1} s^{-1} is the rate constant of the reaction of ${}^1O_2$ with 2-ethylanthracene measured in an independent experiment with photosensitized generation of ${}^1O_2$ in AcOH at 25°C [23, 24].

The integration of Eq. (2) under the condition that hydrogen peroxide is completely consumed after a sufficient lapse of time (i.e., $[H_2O_2]_\infty \approx 0$) gives the equation

$$\frac{[H_2O_2]_0}{[Sub]_0} = 2\left(\eta_\infty - \frac{k_d}{k_s[Sub]_0}\ln(1-\eta_\infty)\right), \qquad (3)$$

where $[H_2O_2]_0$ and $[Sub]_0$ are the initial concentrations of H_2O_2 and the substrate, respectively; $[Sub]_\infty$ is the substrate concentration after the complete consumption of H_2O_2; and $\eta_\infty = \frac{[Sub]_0 - [Sub]_\infty}{[Sub]_0} = 1 - \frac{[Sub]_\infty}{[Sub]_0}$ is the limiting substrate conversion reached after the complete consumption of H_2O_2.

In a particular case when the initial 2-ethylanthracene concentration is $[Sub]_0 = 8.45 \times 10^{-3}$ mol/l (as in an experiment) and $\frac{[Sub]_\infty}{[Sub]_0} = 1/e$, the substrate conversion is $\eta_\infty \approx 0.63$. According to Eq. (3), this value

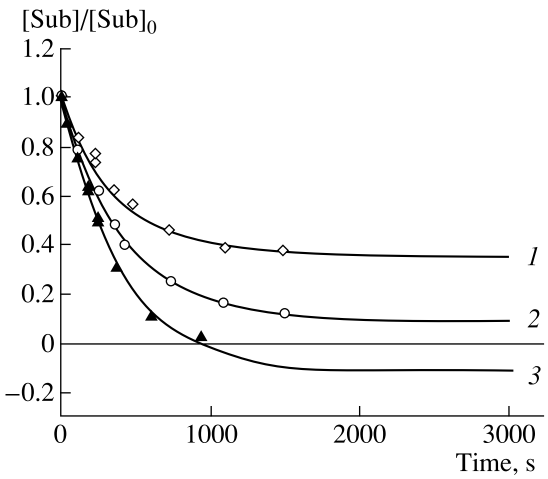


Fig. 3. Kinetic curves for 2-ethylanthracene consumption $\left(\frac{[\mathrm{Sub}]}{[\mathrm{Sub}]_0}\right)$ at different initial concentrations of hydrogen peroxide ($[H_2O_2]_0$). [V] = 5.6 × 10^{-4} mol/l; 34.5°C. (*1*) $[\mathrm{Sub}]_0$ = 0.0208 mol/l; $[H_2O_2]_0$ = 0.082 mol/l; (*2*) $[\mathrm{Sub}]_0$ = 0.0202 mol/l; $[H_2O_2]_0$ = 0.123 mol/l; (*3*) [Sub] = 0.0208 mol/l; $[H_2O_2]_0$ = 0.204 mol/l.

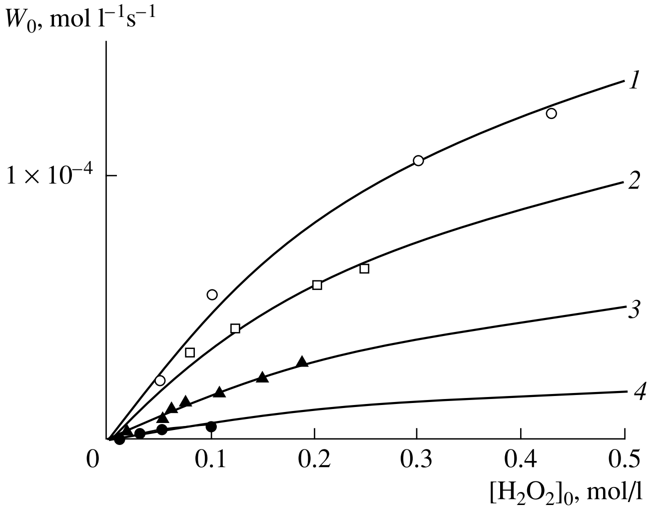


Fig. 4. Initial rates of 2-ethylanthracene consumption vs. the initial concentration of hydrogen peroxide ($[H_2O_2]_0$) at different initial 2-ethylanthracene concentrations. [V] = 5.6 × 10^{-4} mol/l; 34.5°C. (*1*) $[\mathrm{Sub}]_0$ = 0.05 mol/l, (*2*) $[\mathrm{Sub}]_0$ = 0.02 mol/l, (*3*) $[\mathrm{Sub}]_0$ = 0.006 mol/l, and (*4*) $[\mathrm{Sub}]_0$ = 0.001 mol/l.

can be reached at the ratio $\frac{[H_2O_2]_0}{[\mathrm{Sub}]_0}$ = 36. It can be seen in the experimentally constructed plot for the conversion vs. the $\frac{[H_2O_2]_0}{[\mathrm{Sub}]_0}$ ratio (Fig. 1) that the substrate conversion $\eta_\infty \approx 0.63$ is reached at $\frac{[H_2O_2]_0}{[\mathrm{Sub}]_0}$ = 11.7, that is, at a much lower excess of the oxidant. Moreover, the experimental points on the plot of the limiting conversion of 2-ethylanthracene (η_∞) vs. $\frac{[H_2O_2]_0}{[\mathrm{Sub}]_0}$ fall on a straight line, whereas the curve calculated by Eq. (2) monotonically increases and asymptotically approaches unity (Fig. 1).

Table 2. Relative rate constants of the oxidation of alkenes and anthracenes with H_2O_2

Substrate	$k_{\mathrm{Sub}}/k_{\mathrm{A}}$	
	measured*	calculated**
α-Methylstyrene	0.464 ± 0.005	not found***
1,1-Diphenylethylene	0.68 ± 0.01	not found***
trans-1,2-Diphenylethylene	0.145 ± 0.009	not found***
Anthracene	1	1
9-Methylanthracene	1.15 ± 0.05	21
9,10-Dimethylanthracene	15 ± 3	140
9-Phenylanthracene	1.13 ± 0.08	2.8

* Oxidation of H_2O_2 catalyzed by $V^{(V)}$ compounds in AcOH at 30°C.

** For free $^1O_2$ based on the data from [26].

*** The rate of reaction of this substrate with free dissolved $^1O_2$ cannot be estimated because the rate of the reaction between this substrate and $^1O_2$ is lower than the rate of $^1O_2$ quenching with the solvent by a factor of 2 to 3.

These data cast doubt on the hypothesis that dissolved free singlet dioxygen is responsible for oxidation in the test system.

The competitive oxidation of anthracene and its alkyl derivatives was studied to elucidate the nature of the active intermediate. The average values of relative rate constants are presented in Table 2.

The relative rate constant is independent of the substrate conversion. This fact is in line with the oxidation scheme including one active oxidant species, which reacts with all of the substrates. The relative rate constants measured for all of the substrates, except for 9,10-dimethylanthracene, are of the same order of magnitude; however, they are quite different from the published values of reactions of these substrates with free singlet dioxygen dissolved in acetone (Table 2). A comparison of the experimental relative rate constants with the published data suggests that dissolved singlet dioxygen cannot be responsible for the reactions observed in the $H_2O_2/V^{(V)}$/AcOH system.

In addition, substrates like diphenylethylenes and other aryl- or alkyl-substituted alkenes, which are almost inert toward free dissolved $^1O_2$, are readily oxidized in the $H_2O_2/V^{(V)}$/AcOH system (Table 2).

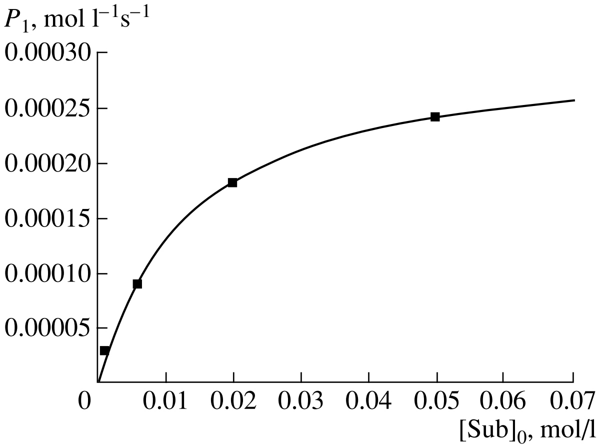


Fig. 5. Parameter P_1 as a function of the initial concentration of 2-ethylanthracene ($[Sub]_0$). [V] = 5.6×10^{-4} mol/l; 34.5°C.

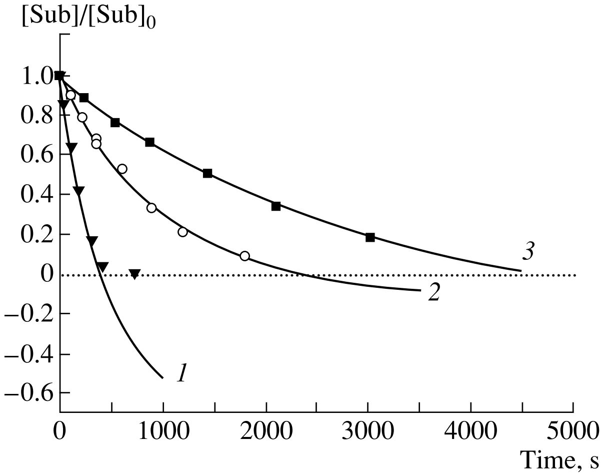


Fig. 6. Kinetic curves for 2-ethylanthracene consumption $\frac{[Sub]}{[Sub]_0}$ at different water concentrations in the reaction solution. $[Sub]_0$ = 0.006 mol/l; $[H_2O_2]_0$ = 0.144 mol/l; [V] = 5.6×10^{-4} mol/l; 34.5°C: (*1*) no water added, (*2*) 1.33 mol/l water added, and (*3*) 3.73 mol/l water added.

All the above data imply that singlet dioxygen is not the only or predominant oxidant species in the system. It seems reasonable that another intermediate of the decomposition of H_2O_2, for example, a vanadium(V) complex formed in the system, is responsible for the substrate oxidation.

To elucidate the pathways of formation of the active oxidant and to evaluate its reactivity, we studied the kinetics of 2-ethylanthracene oxidation with hydrogen peroxide in the presence of vanadium(V) complexes in an AcOH solution.

The consumption of 2-ethylanthracene in the absence of a catalyst from an H_2O_2/AcOH solution was no higher than 10% in 6 h. Therefore, the noncatalyzed substrate oxidation in the test system can be neglected. The initial rate of 2-ethylanthracene oxidation is proportional to the catalyst concentration (Fig. 2).

The consumption of 2-ethylanthracene is adequately described by the following exponential equation with a nonzero asymptote (Fig. 3):

$$\frac{[Sub]_\infty}{[Sub]_0} = A_1 e^{-k_{eff}\tau} + y_0. \quad (4)$$

The position of the asymptote depends on the initial concentrations of the oxidant and the substrate (Fig. 3). Parameter y_0 in Eq. (4) can be negative in a large excess of the oxidant ($[H_2O_2] > 0.2$ mol/l). This fact indicates the zero or near-zero order of the reaction with respect to the substrate concentration.

Addition of 2-ethylanthraquinone has no effect on the rate of 2-ethylanthracene oxidation. Hence, the inhibition of the reaction by the reaction product can be neglected in the kinetic description. Nevertheless, we examined the reaction kinetics using the initial rates of 2-ethylanthracene consumption to avoid possible errors.

At equal substrate concentrations, the initial rates of 2-ethylanthracene oxidation calculated using Eq. (5) increase with increasing the initial concentration of the oxidant, all other factors being the same (Fig. 4).

$$w_0 = \left(-\frac{d[Sub]}{d\tau}\right)_0 = A_1[Sub]_0 k_{eff}, \quad (5)$$

where A_1 and k_{eff} are empirical parameters dependent on the initial substrate, oxidant, water, and catalyst concentrations.

The rate of 2-ethylanthracene consumption at a constant $[Sub]_0$ can be described by a fractional rational function of the form

$$w_0 = \frac{P_1[H_2O_2]_0}{P_2 + [H_2O_2]_0}. \quad (6)$$

The values of parameters P_1 and P_2 for the substrate concentration range 0.001–0.0508 mol/l in four experimental series are given in Table 3.

The variation of parameter P_2 is no higher than the standard deviation in all of the four experimental series. This fact suggests that P_2 is independent of the initial substrate concentration.

The dependence of P_1 on the initial 2-ethylanthracene concentration (Fig. 5) can be approximated by the fractional rational function

$$P_1 = \frac{P_3[Sub]_0}{P_4 + [Sub]_0} \quad (7)$$

with the average values $P_3 = (3.1 \pm 0.2) \times 10^{-4}$ mol l^{-1} s^{-1} and $P_4 = (1.4 \pm 0.2) \times 10^{-2}$ mol/l.

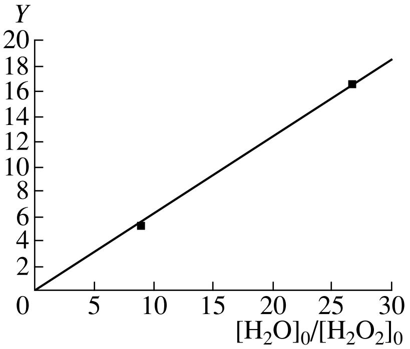


Fig. 7. Straight line in the coordinates Y = $\left\{\frac{[\mathrm{Sub}]_0 P_3}{w_0(P_4 + [\mathrm{Sub}]_0)} - \frac{P_2}{[H_2O_2]_0} - 1\right\}$ and $\left\{\frac{[H_2O]_0}{[H_2O_2]_0}\right\}$, which illustrates the adequacy of Eq. (9) to the chosen mechanistic scheme. $[\mathrm{Sub}]_0 = (5.66–6.64) \times 10^{-3}$ mol/l; $[H_2O_2]_0 = 0.139–0.149$ mol/l; $[V] = 5.6 \times 10^{-4}$ mol/l; 34.5°C.

Hence, the dependence of the initial rate of test reaction (VI) on the initial substrate and oxidant concentrations is described by the Michaelis–Menten equation,

$$w_0 = \frac{P_3[H_2O_2]_0[\mathrm{Sub}]_0}{(P_2 + [H_2O_2]_0)(P_4 + [\mathrm{Sub}]_0)}. \qquad (8)$$

The reaction rates increase with $[H_2O_2]_0$, approaching a limit which depends on the first term in the denominator of Eq. (8). In terms of Michaelis–Menten kinetics, the presence of a limiting value in the kinetic curves (Figs. 3–5) can indicate that all the catalyst is bound in a strong intermediate complex, which is inactive in 2-ethylanthracene oxidation. This can be a complex with hydrogen peroxide or water because water is introduced into the reaction mixture with H_2O_2. To clarify this situation, we investigated the effect of water additives on the kinetics of 2-ethylanthracene oxidation.

Our experiments showed that water additives inhibit 2-ethylanthracene oxidation. However, in this case, the shapes of kinetic curves remained unchanged (Fig. 6). Therefore, the form of Eq. (8) should also be unchanged. The effect of water cannot be explained as competition between H_2O_2 and 2-ethylanthracene for the coordination to the vanadium(V) atom[2]. Therefore, the term responsible for the inhibition of the reaction by H_2O should also be included in the first term of the denominator of Eq. (8):

$$w_0 = \frac{P_3[H_2O_2]_0[\mathrm{Sub}]_0}{(P_2 + P_5[H_2O] + [H_2O_2]_0)(P_4 + [\mathrm{Sub}]_0)} \qquad (9)$$

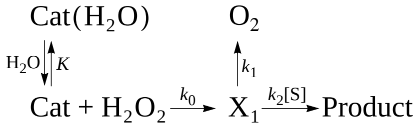
or

$$\frac{[\mathrm{Sub}]_0 P_3}{w_0(P_4 + [\mathrm{Sub}]_0)} - \frac{P_2}{[H_2O_2]_0} - 1 = P_5\frac{[H_2O]_0}{[H_2O_2]_0}, \qquad (10)$$

where $[H_2O]_0$ is the initial concentration of water in mol/l.

Equation (9) adequately describes the experimental data with an average value of $P_5 = 0.62 \pm 0.04$, and the plot in the $\left\{\frac{[\mathrm{Sub}]_0 P_3}{w_0(P_4 + [\mathrm{Sub}]_0)} - \frac{P_2}{[H_2O_2]_0} - 1\right\}$ vs. $\left\{\frac{[H_2O]_0}{[H_2O_2]_0}\right\}$ coordinates is a straight line (Fig. 7).

Two mechanisms (Schemes A, B) can be used to rationalize the kinetic features found. Both of the schemes assume quasi-steady-state concentrations of an active oxidant that forms in the rate-limiting step.



Scheme A.

According to this scheme, the active intermediate X_1, which is responsible for 2-ethylanthracene oxidation and H_2O_2 decomposition, is formed via a reaction between H_2O_2 and the $V^{(V)}$ complex, which is denoted as Cat in Scheme A. According to the ^{51}V NMR data, the complex of $V^{(V)}$ with two peroxo groups $[V^{(V)}O(O_2)_2]^-$ is the predominant species in the reaction solution within the concentration range $[H_2O_2]_0 = 0.1–1$ mol/l. The NMR signals of other $V^{(V)}$ complexes were absent [13]. Hence, Cat in Scheme A designates $[V^{(V)}O(O_2)_2]^-$ and the step of X_1 formation can be depicted by the equation

$$[VO(O_2)_2]^- + H_2O_2 = [V(O_2)_3]^- + H_2O. \qquad (VII)$$

Consequently, in terms of Scheme A, the complex X_1 contains three peroxo groups[3]. $[V(O_2)_3]^-$ and the inhibition of reaction (VI) by water can be attributed to the formation of a strong aqua complex, which cannot, for some reason, be converted into a triperoxo complex. However, the ^{51}V NMR spectra of the reaction solutions with water concentrations up to 2 mol/l exhibit no signals other than those corresponding to the vanadium(V)

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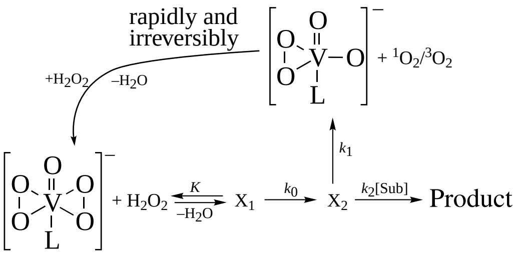
[2] The mechanism of 2-ethylanthracene oxidation involving the intermediate complex of 2-ethylanthracene with a catalyst can be excluded from consideration because there are no experimental data or theoretical reasons indicating the possibility of the existence of these complexes.

[3] The solvent molecules (AcOH or H_2O) in the formulas of tri- and diperoxo complexes are omitted for simplicity.

diperoxo complex, and this fact contradicts the assumption on the formation of a strong aqua complex.



(L is the solvent molecule, H_2O or AcOH)

Scheme B.

According to Scheme B, the triperoxo complex X_1 is formed from the complex $[VO(O_2)_2]^-$, which is predominant in terms of concentration, through the replacement of one oxo ligand. At the rate-limiting step, the complex X_1 transforms into the active intermediate X_2, which can either react with 2-ethylanthracene or decompose with the elimination of the O_2 molecule to form an inactive vanadium compound. In the framework of this scheme, the initial rate of reaction (VI) can be described by the following equation:

$$w_0 = \frac{K[VO(O_2)_2]k_0[H_2O_2]_0[Sub]_0}{([H_2O]'_0 + K[H_2O_2]_0)\left(\frac{k_1}{k_2} + [Sub]_0\right)}. \qquad (11)$$

The total initial concentration of water $[H_2O]'_0$ = $[H_2O]_0$ + $[H_2O]''_0$ + $\alpha[H_2O_2]_0$ includes the concentrations of added water ($[H_2O]_0$), the water contained in the AcOH used ($[H_2O]''_0$ = 0.8 M), and the water introduced into the reaction solution with aqueous 17.8 mol/l hydrogen peroxide ($\alpha[H_2O_2]_0$, where α = 1.64 is the ratio between the concentrations of water and hydrogen peroxide).

On this basis, Eq. (11) takes the form

$$w_0 = \frac{\frac{K[Cat]k_0}{K+\alpha}[H_2O_2]_0[Sub]_0}{\left(\frac{[H_2O]''}{K+\alpha} + \frac{[H_2O]}{K+\alpha} + [H_2O_2]_0\right)\left(\frac{k_1}{k_2} + [Sub]_0\right)}. \qquad (12)$$

From a comparison of Eqs. (9) and (12), we obtain the following values of parameters:

$$P_2 = \frac{[H_2O]''}{K+\alpha}; \quad P_3 = \frac{K[Cat]k_0}{K+\alpha};$$

$$P_4 = \frac{k_1}{k_2}; \quad P_5 = \frac{1}{K+\alpha}.$$

Thus, the value of $P_5 = P_2/[H_2O]''$ is 0.5 ± 0.1 because the concentration of water in the solvent is $[H_2O]''_0$ = 0.8 mol/l. The value of P_5 calculated from independent kinetics data (Eq. (9)) is 0.62 ± 0.05. Both of the values coincide to within the experimental error; this fact supports the adequacy of the kinetic model presented in Scheme B.

Table 3. Parameters of Eq. (6) at different initial 2-ethylanthracene concentrations ($[V] = 5.6 \times 10^{-4}$ mol/l; $[H_2O_2]_0$ = 0.012–0.3 mol/l; AcOH; 34.5°C)

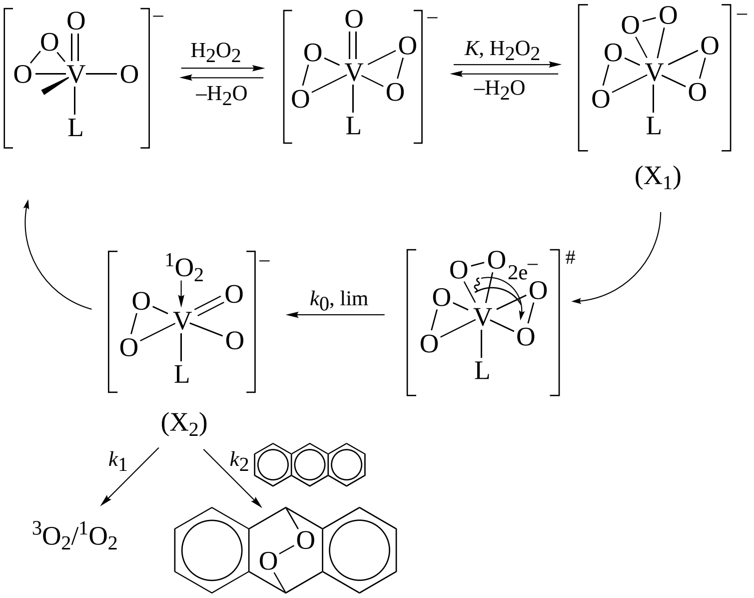
$[Sub]_0$, mol/l	P_1, mol l^{-1} s^{-1}	P_2, mol/l
0.05	$2.6 \times 10^{-4} \pm 8 \times 10^{-6}$	0.5 ± 0.1
0.02	$1.9 \times 10^{-4} \pm 7 \times 10^{-6}$	0.4 ± 0.2
0.006	$1 \times 10^{-4} \pm 2 \times 10^{-6}$	0.5 ± 0.1
0.001	$4 \times 10^{-5} \pm 3 \times 10^{-6}$	0.3 ± 0.2
Average value		0.4 ± 0.1

The equilibrium constant $K = \frac{1}{P_5} - \alpha = -0.03 \pm 0.1$ is much lower than α; therefore, neglecting the corresponding term in the denominator of Eq. (12), we obtain

$$W_0 = \frac{K[Cat]_0[H_2O_2]_0[Sub]_0}{[H_2O]'_0\left(\frac{k_1}{k_2} + [Sub]_0\right)}. \qquad (13)$$

According to Eq. (13), the occurrence of a limiting value on the kinetic curves for reaction (VI) (Fig. 4) with increasing $[H_2O_2]_0$ can be attributed to a parallel increase in the concentration of water that is introduced into the reaction mixture with hydrogen peroxide. Because H_2O_2 and H_2O molecules compete with each other for a coordination site at the $V^{(V)}$ atom, the concentration of the triperoxo complex is expected to be lower than that with the use of water-free H_2O_2. This suggestion is also in line with the ^{51}V NMR data, which demonstrate the predomination of $V^{(V)}$ diperoxo complexes in the course of the reaction.

Thus, according to the data obtained, the intermediate complex X_1 is formed from the diperoxo complex $[VO(O_2)_2]^-$ through the addition of an H_2O_2 molecule and the elimination of an H_2O molecule. In this reaction, the oxygen atom of the vanadyl group (VO) in the diperoxo complex is replaced with a peroxo group to form the triperoxo complex (Scheme 2).



Scheme 2. Mechanism of singlet dioxygen transfer to an anthracene molecule.

In terms of Scheme 2, the complex X_2 of vanadium(V) with singlet dioxygen is responsible for 2-ethylanthracene oxidation.

The transformation of the intermediate complex X_1 into the active oxidant X_2 likely involves the transfer of two electrons between two coordinated peroxo groups (in one step or in two successive one-electron steps). The inner-sphere formation of an excited dioxygen molecule is accompanied by the formation of two rather strong groups $V^{(V)}{=}O$ and $(V^{(V)}–O)^-$. The kinetic data do not allow us to judge the composition and structure of the active oxidant species in more detail. However, we can state with assurance that free singlet dioxygen is not the active oxidant species, and a vanadium(V) complex is the species that transfers a singlet dioxygen molecule to an anthracene molecule.

This is also supported by the following fact. Processing the initial reaction rates as functions of the initial 2-ethylanthracene concentration (Fig. 4) using Eq. (6), we can calculate parameter P_4. In the framework of Scheme 2, this parameter is equal to the k_1/k_2 ratio (k_1 is the rate constant of X_2 deactivation, and k_2 is the rate constant of 2-ethylanthracene oxidation) and its value is 0.014. From independent experiments on 2ethylanthracene photooxidation with dioxygen in AcOH solution [23, 24], we obtained a ratio of the rate constant of $^1O_2$ quenching (deactivation) to the rate constant of $^1O_2$ addition to the 2-ethylanthracene molecule equal to 0.15. A comparison of these ratios shows that the kinetic parameters related to X_2 differ remarkably from those for free $^1O_2$. Moreover, X_2 was found to be a much more effective oxidant toward 2-ethylanthracene than free $^1O_2$ dissolved in the same solvent.

If the spin conservation rule is applicable to the transition $X_1 \longrightarrow X_2$, the molecule of dioxygen formed should be in a singlet state. Thus, the spin conservation rule favors the route leading to the formation of the exciplex X_2 containing $^1O_2$ as a ligand through the disproportionation of two O_2^{2-} ligands of the complex $[V^{(V)}(O_2)_2]^-(X_1)$. The inner-sphere transfer of two electrons from an O_2^{2-} group to another, which results in the formation of the active species X_2 (Scheme 2), is an example of a redox reaction catalyzed by a metal with d^0 nonbonding configuration [7].

CONCLUSION

The nature of the active species responsible for the transfer of singlet dioxygen from H_2O_2 to a substrate molecule in the $H_2O_2/V^{(V)}$/AcOH oxidative system was elucidated in this study. It follows from the kinetic data obtained that at least 95% of 2-ethylanthracene is oxidized via the reaction with a vanadium(V) complex containing the $^1O_2$ molecule as a ligand. Thus, coordinated $^1O_2$ rather than free singlet dioxygen is the active oxidant in the test system.

Alkene exciplexes, that is, alkene complexes with electronically excited species like singlet dioxygen, are well known from the works of Adam and coauthors [27, 28]. Data on the photoinduced oxidation of alkenes containing an H atom at the allyl position unambiguously suggest that the reaction occurs via the formation of an intermediate π-complex between $^1O_2$ and an alkene molecule. Intermediates of this type are responsible for the reaction stereoselectivity [29].

The $V^{(V)}(^1O_2)$ exciplex postulated in this work differs from the Adam exiplexes in that the vanadium(V) ion cannot be an electron donor. In this case, the $^1O_2$ molecule can be stabilized by the donation of its electron pair to the vacant *d* orbital of the vanadium ion. The interaction of the π-antibonding orbital of $^1O_2$ with the electrons of other ligands and with the vacant *d* orbital of the $V^{(V)}$ ion should be taken into account in the discussion of the stability and reactivity of the $V^{(V)}(^1O_2)$ complex.

The complex X_2 can be more efficient in 2-ethylanthracene oxidation than free singlet dioxygen dissolved in the reaction mixture in the following two cases:

(1) The rate constant of the reaction of the complex X_2 with 2-ethylanthracene is higher than the corresponding constant for free $^1O_2$.

(2) The lifetime of the complex X_2 is longer than that of $^1O_2$ in the same solution.

The formation of a $V^{(V)}$ complex with $^1O_2$ due to the donor–acceptor interaction of the filled π* orbital of $^1O_2$ with the vacant *d* orbital of the central atom should enhance the electrophilicity of the coordinated $^1O_2$. On the other hand, the interaction of the filled π* orbital of the O_2^{2-} ligand with the vacant π* orbital of the coordinated $^1O_2$ having the same symmetry with the participation of the vacant *d* orbital of $V^{(V)}$ also seems conceivable. Such an interaction can increase the electron density on the π* orbital of the coordinated $^1O_2$ and decrease its electrophilicity. Thus, both the lifetime and the reactivity of a coordinated $^1O_2$ molecule can depend on the ligand environment, the solvent composition, and the nature of the metal.

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