

Free Radical/Singlet Dioxygen System under the Conditions of Catalytic Hydrogen Peroxide Decomposition

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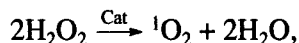
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Abstract—Hydrogen peroxide decomposition and the oxidation of unsaturated compounds (anthracenes, alkenes, etc.) in the $\text{H}_2\text{O}_2/\text{V}^{(\text{V})}/\text{AcOH}$ system occur via a molecular mechanism. H_2O_2 decomposes to yield singlet dioxygen $^1\text{O}_2(^1\Delta_g)$. Among $\text{V}^{(\text{V})}$ peroxo complexes of different compositions, coordinated superoxide radical anions $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ are found in a steady-state concentration in the system under investigation. Styrene oxidation in the $\text{H}_2\text{O}_2/\text{V}^{(\text{V})}/\text{AcOH}$ system unusually accelerates in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT), which is an inhibitor of radical chain reactions. This is explained by a decrease in the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ concentration and an increase in the concentration of dissolved $^1\text{O}_2$ in the presence of ionol. A new phenomenon in the chemistry of singlet dioxygen is found: the ESR signal from the paramagnetic system upon its interaction with $^1\text{O}_2$ broadens in an unusually drastic manner (up to 10 G). This broadening is virtually independent of the nature of the radicals, the acidity of the medium, and the nature of the metal catalysts used for the generation of $^1\text{O}_2(^1\Delta_g)$.

INTRODUCTION

Free-radical oxidation reactions with oxygen-centered radicals as chain-transfer agents are widely known [1]. Singlet dioxygen $^1\text{O}_2(^1\Delta_g)$ is known as an active oxidant in chemical and biological systems [2, 3]. The interaction between singlet dioxygen and oxygen-containing radical species, which are active oxidants, should be taken into account when studying oxidation systems where they are present (see, for example, [4, 5]).

The photophysical generation of singlet dioxygen $^1\text{O}_2(^1\Delta_g)$ via the energy transfer from an excited photosensitizer molecule to an $^3\text{O}_2$ molecule is used most widely. One of the chemical sources of $^1\text{O}_2$ is peroxy radical recombination [4]. The reaction of superoxide radical anions with halocarbons also yields $^1\text{O}_2$ [5]. In recent years, a method is being developed for producing $^1\text{O}_2(^1\Delta_g)$ by the catalytic decomposition of alkyl hydroperoxides [6] or hydrogen peroxide [7–11] to form active species capable of generating $^1\text{O}_2$ or transferring it to substrates:



where Cat = $\text{Ca}(\text{OH})_2$, H_2TiO_3 , NaVO_3 , Na_2MoO_4 , Na_2WO_4 , etc.

In this article, we report experimental results indicating the ability of radicals to retard the oxidation of organic substrates in the catalytic systems with singlet dioxygen as an active oxidant (see Subsection 1.3). This finding stimulated us for further research into the

interaction of radicals with $^1\text{O}_2$. The results obtained are presented in Section 2.

EXPERIMENTAL

Reagents and Materials

Acetic acid, toluene, benzene, hexadecane, decane, and aqueous hydrogen peroxide (9.67 mol/l), all chemically pure, were used without additional purification. A concentrated (15 mol/l) solution of H_2O_2 was obtained by distillation of commercially available H_2O_2 (analytically pure). 1-Hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, and styrene, all analytically pure, were distilled before experiments; the purity was controlled by GLC. *trans*-Stilbene, anthracene, and 9,10-dimethylantracene (all containing at least 95% of the main substance according to GLC) and NH_4VO_3 were used without additional purification. $\text{VO}(\text{acac})_2$ was recrystallized from CHCl_3 .

Preparation of a Catalyst Solution

A solution of $\text{V}^{(\text{V})}$ in AcOH was prepared by the treatment of 100 mg finely divided NH_4VO_3 with 100 ml boiling AcOH for 4–5 h. Undissolved NH_4VO_3 was filtered off. The $\text{V}^{(\text{V})}$ content of the solution was determined using an ICP-MS HP 4500 spectrometer with NH_4VO_3 as an external standard and found equal to 3.7×10^{-3} mol/l. Some kinetic experiments were car-

ried out with a catalyst based on $\text{VO}(\text{acac})_2$, whose solubility in AcOH is much higher. The ESR signal from $\text{V}(\text{IV})$ in $\text{VO}(\text{acac})_2$ disappears as soon as H_2O_2 is added to the reaction solution. The replacement of $\text{VO}(\text{acac})_2$ by NH_4VO_3 did not affect the composition of the reaction products and the reaction rate.

Decomposition of H_2O_2

The reaction was carried out at 30°C in a temperature-controlled Pyrex glass reactor equipped with a reflux condenser and a magnetic stirrer. In a typical run, 4.4 ml (42.5 mmol) of a 9.67 mol/l H_2O_2 aqueous solution was added to 1.33 mg (0.005 mmol) $\text{VO}(\text{acac})_2$ in 5 ml AcOH . In the investigation of the effect of an inhibitor on the rate of H_2O_2 decomposition, the inhibitor was dissolved in the reaction mixture before the addition of H_2O_2 . Samples taken from the reaction mixture were diluted with 3 ml of a 2N H_2SO_4 aqueous solution. The rate of H_2O_2 decomposition was determined by iodometric titration.

Oxidation of Alkenes and Anthracenes and the Analysis of the Reaction Products

The oxidation of alkenes was carried out at 30°C in a temperature-controlled glass reactor equipped with a reflux condenser and a magnetic stirrer. In a typical run, 0.52 ml (5 mmol) of a 9.67 mol/l H_2O_2 aqueous solution was added to a solution of 13.6 mg (0.01 mmol) $\text{VO}(\text{acac})_2$ and 42 mg (0.5 mmol) 1-hexene in 5 ml glacial AcOH .

The oxidation of styrene in the presence of BHT (2,6-di-*tert*-butyl-4-methylphenol) was carried out under the conditions described above. In a typical run, 0.52 ml (5 mmol) of a 9.67 mol/l H_2O_2 aqueous solution was added to a 10^{-3} mol/l $\text{V}(\text{V})$ complex solution in 10 ml glacial AcOH containing 57 μl (0.5 mmol) styrene and 5.5 mg (0.0025 mmol) BHT. Current H_2O_2 concentrations were determined by iodometric titration. The conversion of substrates and the reaction yield were determined by GLC using a 3700 chromatograph (Russia) equipped with a capillary column (0.2 mm \times 25 m, 0.33 μm HP-1), a FID, and an ITs-26 integrator (Bulgaria). An internal standard (1 ml of an 1% benzene solution in toluene in the runs with 1-hexene or *n*-decane in the runs with styrene) was added to 1 ml of the reaction solution after the complete decomposition of H_2O_2 before chromatographic analyses. An organic phase was washed out with water (2×3 ml) and 5% Na_2CO_3 aqueous solution (3 ml).

The chromatographic analysis of styrene was carried out under the following conditions: $T_{\text{inj}} = 200^\circ\text{C}$, $P = 1$ atm, split 1 : 40, $T_{\text{col}}^{\text{init}} = 100^\circ\text{C}$ (2 min), $T_{\text{col}}^{\text{final}} = 170^\circ\text{C}$ (2 min), and a heating rate of $10^\circ\text{C}/\text{min}$.

The oxidation of 9,10-dimethylanthracene was carried out as described above. In a typical run, 1.1 ml (10.7 mmol) of a 9.67 mol/l H_2O_2 aqueous solution was

added to a solution of 53 mg (0.2 mmol) $\text{VO}(\text{acac})_2$ and 0.3 g (1.46 mmol) 9,10-dimethylanthracene in 20 ml glacial AcOH . Upon H_2O_2 exhaustion, water (100 ml) was added to the reaction solution. Water-insoluble organic compounds were extracted with benzene (2×20 ml). The extracted substance was washed out with 20 ml of a 5% Na_2CO_3 aqueous solution and dried over MgSO_4 . The solvent was evaporated under vacuum at 20°C . Yellow crystalline product **I** was separated from the by-products (9,10-anthraquinone and a red polymeric compound) by column chromatography on silica gel with 5% diethyl ether in hexane as an eluent. The yield of the target product was 72% (0.25 g, 4.05 mmol).

The chromatographic analysis of anthracene and its derivatives was carried out under the following conditions: $T_{\text{inj}} = 270^\circ\text{C}$, $P = 1.5$ atm, split 1 : 40, $T_{\text{col}}^{\text{init}} = 220^\circ\text{C}$ (2 min), $T_{\text{col}}^{\text{final}} = 270^\circ\text{C}$ (2 min), and a heating rate of $10^\circ\text{C}/\text{min}$.

The iodometric titration was done as follows. Dry ice (~5 g), the product (40.2 mg) (0.212 mmol), and NaI (1 g) were added successively to 10 ml glacial AcOH . The mixture was allowed to stay for 1 h at 50 – 60°C in Ar flow. Once the mixture was cooled to room temperature, the I_2 formed was titrated with 0.101 N $\text{Na}_2\text{S}_2\text{O}_3$. Upon conversion to 9,10-epidioxy-9,10-dimethylanthracene, the active oxygen content of **I** was equal to 4.20×10^{-3} mmol/mg.

Spectral Measurements

NMR spectra were recorded at 20°C using a Bruker AM 400 instrument. The ^1H NMR spectrum of **I** in CDCl_3 , displayed the following signals (ppm): 1.48 (singlet, 3H) and 7.2 and 7.4 (both multiplets of the AA'BB' system, 2H). Its ^{13}C NMR spectrum in CDCl_3 (with the ^1H suppression) displayed the following signals (ppm): 18 (quadruplet), 80 (singlet), 120 (doublet), 130 (doublet), and 142 (singlet). The ^{13}C NMR spectrum of 9,10-epidioxy-9,10-dimethylanthracene obtained using the ACD-CNMR simulation package displayed the following signals (ppm): 15.8 (quadruplet), 80 (singlet), 119 (doublet), 129 (doublet), and 138 (singlet). According to the NMR data, the yield of **I** was ~90%.

The GC-MS analysis of **I** was carried out on a AUTOMASS-150 instrument (Delsi Nermag, France) with a capillary column 0.25 mm \times 25 m, 0.33 μm OV-1 (Rescom). The analytic conditions were as follows: $T_{\text{inj}} = 270^\circ\text{C}$, $P = 1.5$ atm, split 1 : 40, $T_{\text{col}}^{\text{init}} = 150^\circ\text{C}$ (2 min), $T_{\text{col}}^{\text{final}} = 250^\circ\text{C}$ (2 min), and a heating rate of $10^\circ\text{C}/\text{min}$; the carrier gas was helium. The chromatogram involved three peaks with the retention times (RTs) 4 : 29, 5 : 12, and 5 : 49 min. The peak with an RT of 4 : 29 min was assigned according to its mass spectrum (using the NIS/NIH library) to 9,10-anthraquinone (~10% yield). The mass spectra of the two other substances (the RTs 5 : 12 and 5 : 49 min) were not found

in the library. These substances were identified by their fragmentation patterns as 9,10-dimethyl-9,10-dioxanthracene (**Ia**) and 9,10-dimethoxyanthracene (**Ib**), respectively. The yields of these products were at most 1–2%. It is likely that, during GC–MS analysis, 9,10-dimethyl-9,10-epidioxanthracene (**I**) decomposed into nonvolatile products and small amounts of **Ia** and **Ib**.

MS-EI (70 eV) for **Ia**, m/e : 225, 210, 208, 180, 152 (PP), 105, 76, and 63. (Hereafter, PP means principal peak.)

MS-EI (70 eV) for **Ib**, m/e : 238 (PP), 195, 165, 152, 132, 115, 89, 77, 75, 63, and 43.

ESR spectra were recorded at 255–293 K on a Radiopan SE/X-2542 instrument (at 9450 MHz and a modulation amplitude of 0.5 G) using 1,1-diphenyl-2-picrylhydrazide (DPPH) as an internal standard. The spectra were processed on computer and simulated according to the procedure described in [12]. The integral intensity of a signal was determined relative to the 3rd and 4th components of the signal from Mn^{2+}/MgO used as an internal standard.

In a typical run, 1 ml (9.7 mmol) of a 9.67 mol/l H_2O_2 aqueous solution was added to a 10^{-2} mol/l $VO(acac)_2$ solution in 9 ml glacial AcOH. The mixture was placed in a cell of the ESR spectrometer with an inner diameter of 5 mm equipped with two glass capillaries with a diameter of 0.2–0.3 mm. The capillaries were connected to chambers filled with O_2 , Ar, or CO_2 , which passed through the cell during ESR measurements.

Phosphorescence spectra of 1O_2 formed by H_2O_2 decomposition in AcOH in the presence of $V^{(V)}$ compounds were measured in the photon-counting regime using an electronic system for recording one-photon pulses. We used the recording system of a laser phosphorescence meter described in [13] consisting of an MC-80 monochromator and an FEU-83-cooled photoelectric multiplier. A lens converging radiation from the cell and an IKS-3 light filter were placed before the monochromator. The spectral width of the monochromator slit was equal to 16 nm. One-photon pulses amplified by the photoelectric multiplier were fed to the input of an S1-75 oscillograph operating as a discriminator. Only pulses triggering the slave sweep of the oscillograph were taken into account. The sweep-triggering threshold level was selected so that the signal-to-noise ratio was maximal. The signal from the sweep synchronization output was supplied to the input of an NTA-1024 analyzer operating as a multichannel pulse counter.

In the experiments, the sweep speed of the monochromator was 15 nm/min, and the channel time of the analyzer was 2 s, which corresponded to 0.5 nm per channel. Spectra measured by the analyzer were smoothed by three points and, after removal of a part of the points, corrected for the spectral sensitivity of the recording system calibrated using a standard lamp,

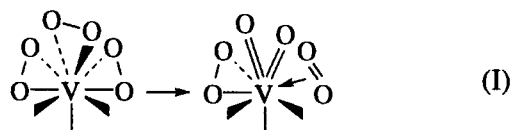
which is supplied together with a Perkin-Elmer fluorimeter. The mathematical processing was fully computerized and carried out on a personal computer using the GraFit software package.

In a typical run, 0.18 ml (3.06 mmol) of a 17 mol/l H_2O_2 aqueous solution was added to a 10^{-2} mol/l $VO(acac)_2$ solution in 3 ml glacial AcOH. The mixture was placed in a glass cell (1×3 cm). The chemiluminescence spectrum was recorded at 22°C.

RESULTS AND DISCUSSION

1. $V^{(V)}/H_2O_2/AcOH$ System

1.1. $V^{(V)}(O_2^{\cdot-})$ paramagnetic complex and singlet dioxygen. Singlet dioxygen or its complex with the catalyst¹ formed by the catalytic decomposition of H_2O_2 can be an active species responsible for substrate consumption in the oxidation reaction. For example, in hydrogen peroxide decomposition in the $V^{(V)}/H_2O_2/AcOH$ system, vanadium(V) complexes are formed, which are capable of transferring singlet dioxygen from H_2O_2 to an organic substrate molecule [8–11]. Kinetic studies of this system showed that the complex with three peroxo groups, $V(O_2^{\cdot-})_3$, is the main precursor of 1O_2 . A vanadium complex with singlet dioxygen as a ligand directly responsible for the transfer of 1O_2 is probably formed by the intraspheric redox dismutation of two peroxo groups of the $V(O_2^{\cdot-})_3$ complex [8–11]:



In the absence of suitable substrates, 1O_2 is accumulated in the reaction solution as suggested by the phosphorescence spectrum with a characteristic maximum at 1275 nm registered during hydrogen peroxide decomposition in AcOH containing $V^{(V)}$ complexes (Fig. 1).

Apart from diamagnetic active intermediates (vanadium peroxo complexes, the complex with singlet dioxygen, and singlet dioxygen itself), a paramagnetic complex was found in the considered system; the parameters of its ESR spectrum ($g = 2.01125 \pm 0.00005$ G and $a_V = 0.00044$ cm⁻¹) coincide with those for the complex of $V^{(V)}$ with the superoxide radical anion as a ligand,

¹ Hereafter, by a singlet dioxygen complex is meant an intermediate responsible for the transfer of a singlet dioxygen molecule to the oxidation substrate or responsible for the formation of $^1O_2(^1\Delta_g)$ in the solution. The nature of the bond between the O_2 ligand leaving the coordination sphere as 1O_2 and the central atom will be considered separately.

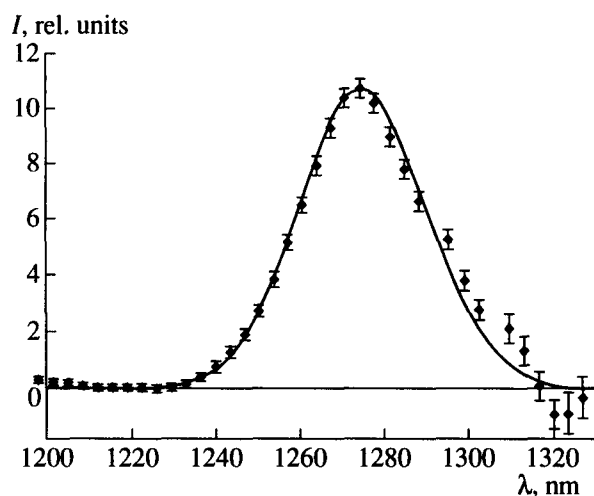


Fig. 1. The phosphorescence spectrum of singlet dioxygen measured during H_2O_2 decomposition in the $\text{H}_2\text{O}_2/\text{V}^{(\text{V})}/\text{AcOH}$ catalytic system ($[\text{V}^{(\text{V})}] = 10^{-2}$ mol/l and $[\text{H}_2\text{O}_2]_0 = 1$ mol/l) at 20°C . $\text{VO}(\text{acac})_2$ was used as a catalyst precursor. Points represent smoothed experimental data; the curve represents the approximation of the experimental data by Gaussian distribution. A constant dark background is subtracted.

$\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ (II), reported in [14–16] (Fig. 2). The concentration of this radical is a steady-state value and decreases as H_2O_2 is consumed.

The rate of hydrogen peroxide decomposition in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system and the shape of the H_2O_2 consumption curve do not change in the presence of the inhibitors of radical processes (Fig. 3). In the reaction solutions containing phenanthroline, acetylacetone, styrene, 2,6-di-*tert*-butyl-4-methylphenol, anthracene, 2-ethylantracene, or 2,6-di-*tert*-butyl-4-dibenzo-1-metoquinone, organic peroxy radicals were not found by ESR. The absence of the respective ESR signals shows that the concentrations of organic radicals are at most 10^{-5} – 10^{-6} mol/l. The anthracene radical cation was not found either during the oxidation of anthracene in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system [8–11]. According to GS-MS, GLC, and ^1H NMR data, anthrone and bianthrone were absent from the products of anthracene oxidation. All these facts suggest that active species generated in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system neither oxidize substrates by the one-electron mechanism nor initiate the chain radical decomposition of H_2O_2 .

In the absence of radical traps (anthracene, BHT, and *p*-nitrozo-*N,N*-dimethylaniline), the integral intensity of the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ signal changes together with H_2O_2 consumption (compare Figs. 3 and 4). In the presence of anthracene or other inhibitors, the integral intensity of the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ signal vs. time has a maximum (Fig. 4). However, kinetic curves for hydrogen peroxide decom-

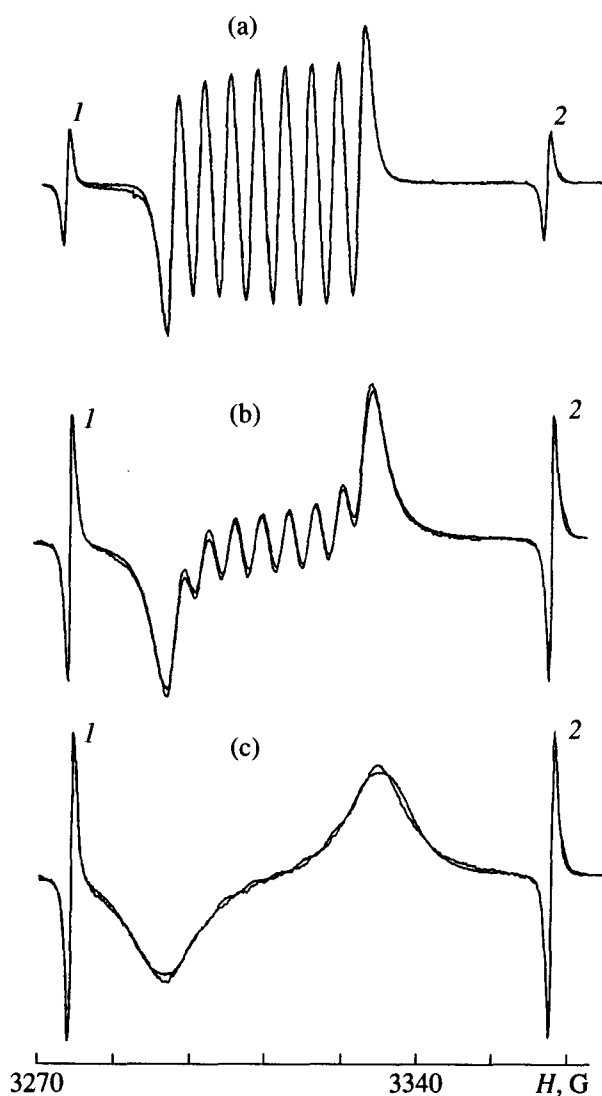


Fig. 2. The ESR spectra of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system ($[\text{V}^{(\text{V})}] = 10^{-2}$ mol/l and $[\text{H}_2\text{O}_2]_0 = 1$ mol/l) measured at 20°C upon (a) Ar and (b) O_2 blowing through the reaction solution and (c) without blowing; the (1) third and (2) fourth components of the ESR signal from $\text{Mn}^{2+}/\text{MgO}$ used as an internal standard.

position and 2-ethylantracene consumption have no induction periods (Figs. 3, 5). Therefore, we suggest a molecular (nonradical) character of the reactions.

Thus, all the kinetic data (the shape of kinetic curves presented in Figs. 3 and 5 and the fact that the rate of H_2O_2 decomposition is unaffected by the inhibitors) suggest that $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radicals are not involved in the chain transfer in the reaction under study. Moreover, this suggestion finds support in analysis of the effects of different factors on the rate of H_2O_2 decomposition and the integral intensity of the ESR signal from the complex radical.

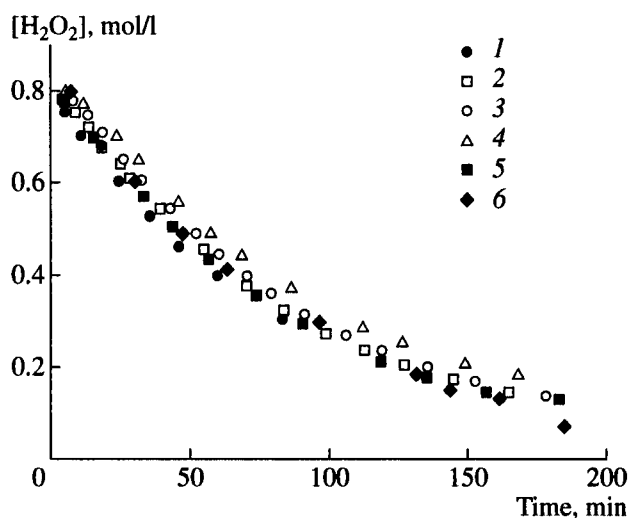


Fig. 3. H_2O_2 decomposition in the presence of inhibitors of radical reactions: (1) ionol (2×10^{-3} mol/l), (2) Pyrex glass powder, (3) *p*-nitroso-*N,N*-dimethylaniline (2×10^{-3} mol/l), (4) anthracene (2×10^{-3} mol/l), (5) without an inhibitor, and (6) anthraquinone (2×10^{-3} mol/l). $[\text{V}^{(\text{V})}] = 10^{-2}$ M, $[\text{H}_2\text{O}_2]_0 = 1$ M, $T = 30^\circ\text{C}$; the solvent, AcOH.

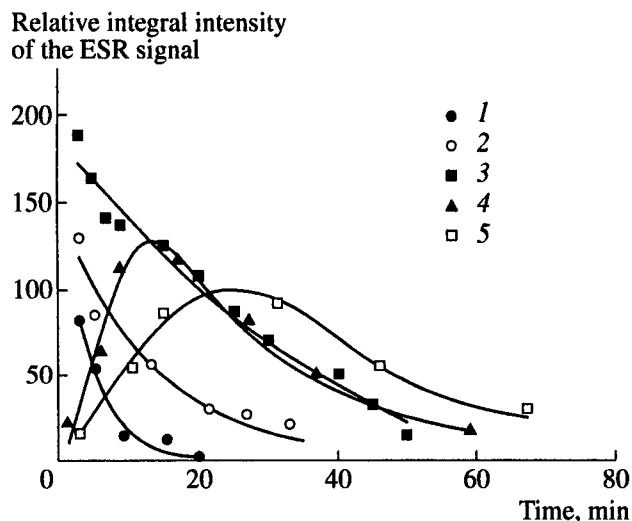


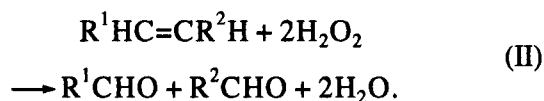
Fig. 4. The relative integral intensity of the ESR signal of $\text{V}^{(\text{V})}(\text{O}_2^\cdot)$ vs. time during H_2O_2 decomposition in AcOH in the presence of $\text{V}^{(\text{V})}$ complexes ($[\text{V}^{(\text{V})}] = 10^{-2}$ mol/l and $[\text{H}_2\text{O}_2] = 1$ mol/l) at 20°C in a Pyrex glass cell with an inner diameter of (1) 1.5 and (2) 5 mm, (3) in a quartz cell with an inner diameter of 5 mm, and in the presence of (4) 2-ethylanthracene (10^{-3} mol/l) and (5) *p*-nitroso-*N,N*-dimethylaniline (2×10^{-3} mol/l).

For example, when using quartz reactor instead of a Pyrex reactor, the rate of H_2O_2 decomposition remained unchanged (Fig. 3), whereas the intensity of the $\text{V}^{(\text{V})}(\text{O}_2^\cdot)$ signal was higher, and the rate of its consumption was lower (Fig. 4). The rate of H_2O_2 decom-

position remained unchanged upon the addition of glass (Pyrex) powder to the reaction mixture (Fig. 3). The concentration of $\text{V}^{(\text{V})}(\text{O}_2^\cdot)$ and its lifetime dramatically decreased with an increase in the surface-to-volume ratio, for example when ESR spectra were recorded with an ampule of a smaller diameter (Fig. 4). Anthracene and ionol had no effect on the rate of H_2O_2 decomposition (Fig. 3) but drastically decreased the initial concentration of $\text{V}^{(\text{V})}(\text{O}_2^\cdot)$ and affected the shape of kinetic curves for radical consumption (Fig. 4).

Thus, the concentration of the paramagnetic complex and the rate of H_2O_2 decomposition depend on various parameters in a different manner (Table 1). Our results suggest that H_2O_2 decomposition in AcOH in the presence of vanadium complexes occurs via a molecular mechanism.

1.2. Oxidation of alkenes. The oxidation of a number of alkenes—1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, cyclohexene, styrene, and *trans*-stilbene—in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system was studied. It was found that for all alkenes except cyclohexene, the $>\text{C}=\text{C}<$ bonds break with the formation of the corresponding aldehydes (Table 2):



In the case of styrene, styrene oxide is one of the main products of radical oxidation [1], but neither styrene oxide nor 2-phenyl-1,2-ethanediol were found in the oxidation products. Moreover, styrene oxide and ethylene glycol were found to be highly resistant to oxidation in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system; they were consumed very slowly. All these findings suggest that epoxides and glycols are not intermediate products in the reaction of interest. In the studied system, benzaldehyde was slowly consumed and benzoic acid was not formed. The absence of the acid from the reaction products and a rather high stability of benzaldehyde suggest a nonradical nature of active species responsible for the reactions in the system.

In cyclohexene oxidation by hydrogen peroxide in the solutions of $\text{V}^{(\text{V})}$ compounds in acetic acid, cyclohexene oxide and the corresponding glycol were absent from the reaction products. Adipic dialdehyde was not found either. The conversion of the alkene was minor. The main reaction occurred as allylic oxidation to form 3-cyclohexenol and 3-cyclohexenone, similarly to the reaction of cyclohexene in acetone or *tert*-butanol in the presence of V_2O_5 [17, 18]:

Table 1. The influence of different factors on the rate of H_2O_2 decomposition and the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radical concentration

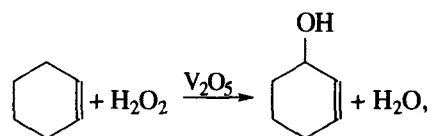
Factor	H_2O_2 decomposition rate	$[\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})]$
Material of the reactor walls	Unaffected	Affected
Surface–volume ratio	"	"
Anthracene	"	"
BHT	"	"

Table 2. The $\text{V}^{(\text{V})}$ -catalyzed oxidation of olefins with hydrogen peroxide in AcOH at 20°C

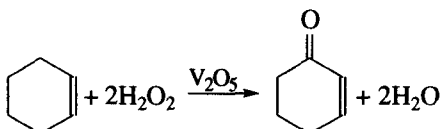
Substrate*	$[\text{H}_2\text{O}_2]_0$, mol/l	$[\text{VO}(\text{acac})] \times 10^2$, mol/l	Substrate conversion, %	RCHO yield**, %	$[\text{H}_2\text{O}_2] \times 10^2$, mol/l***
3-Methyl-1-pentene (0.092)	0.5	1.02	<5	1.7	0.4 (1.7)
4-Methyl-1-pentene (0.10)	0.5	0.88	<5	2.1	0.5 (1.8)
1-Hexene (0.10)	0.5	1.00	<5	1.3	0.5 (1.8)
1-Hexene (0.10)	1.0	0.95	6.4	2.9	0.8 (1.8)
Cyclohexene (0.10)	1.0	1.01	<5	<0.1	0.4 (2.4)
<i>trans</i> -Stilbene (0.10)	0.97	1.09	72	51	0.6 (2.0)
<i>trans</i> -Stilbene (0.089)	0.5	0.92	48	38	0.8 (1.8)
Styrene (0.10)	1.0	1.06	65	40	0.4 (1.8)
Styrene (0.10)	0.5	1.20	41	29	0.4 (1.8)

* Substrate concentrations (mol/l) are given in parentheses.

** The RCHO yield relative to the substrate charge.

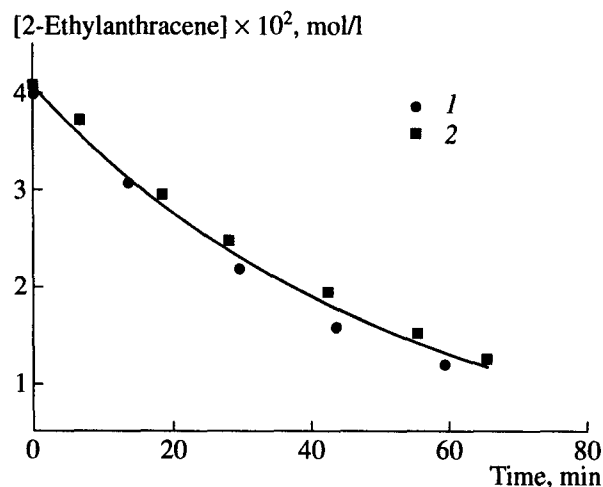
*** The final H_2O_2 concentration. Reaction durations (h) are given in parentheses.

(III)

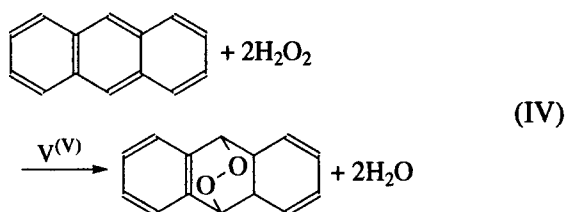


Acyclic aliphatic alkenes (1-hexene, 3-methyl-1-pentene, and 4-methyl-1-pentene) yield the corresponding aldehydes (reaction (II)) in the course of destructive oxidation. However, in the oxidation system, the reactivity of these alkenes was much lower than for the oxidation in organic solvents and water with the formation of corresponding epoxides and glycols [17, 18]. By contrast to aliphatic alkenes, the oxidative cleavage of the double bond $>\text{C}=\text{C}<$ in styrene and *trans*-stilbene occurred under mild conditions (at 20°C), and the conversion of the aromatic alkenes reached 50–70% (for ~2 h), the oxidant/substrate ratio being the same. The fact that the reactivity of alkenes containing aromatic residues is higher than that for alkyl-substituted alkenes suggests that the alkene-attacking active oxidant has electrophilic properties.

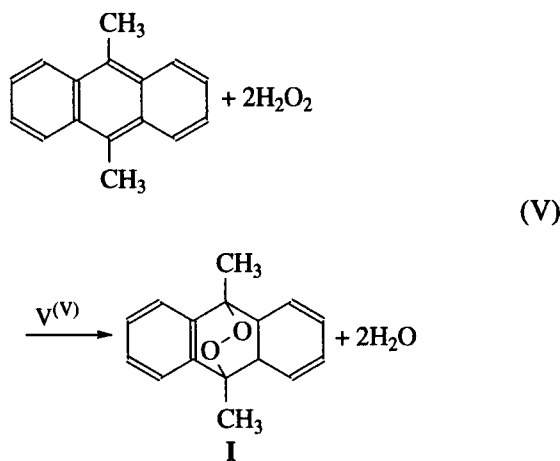
The anthracene oxidation with hydrogen peroxide in AcOH in the presence of $\text{V}^{(\text{V})}$ resulted in anthraquinone in a nearly 100% yield; in this case, gaseous oxygen was not virtually evolved [8]. Using the ^1H NMR and GC–MS techniques, 9,10-dihydro-9,10-

**Fig. 5.** The influence of BHT on the oxidation of 2-ethylanthracene in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system ($[\text{V}^{(\text{V})}] = 10^{-2}$ mol/l and $[\text{H}_2\text{O}_2]_0 = 1$ mol/l) at 20°C: (1) without BHT and (2) $[\text{BHT}] = 2 \times 10^{-3}$ mol/l.

epidioxyanthracene was found to be the primary product of anthracene oxidation [8–11]:



Moreover, in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system, 9,10-dimethylantracene smoothly converted to 9,10-dimethyl-9,10-epidioxyanthracene (I) (at 20°C, the endoperoxide was formed in a 70–90% yield within ~1 h):



The formation of the endoperoxide is one of the tests for the participation of singlet dioxygen in the reaction.

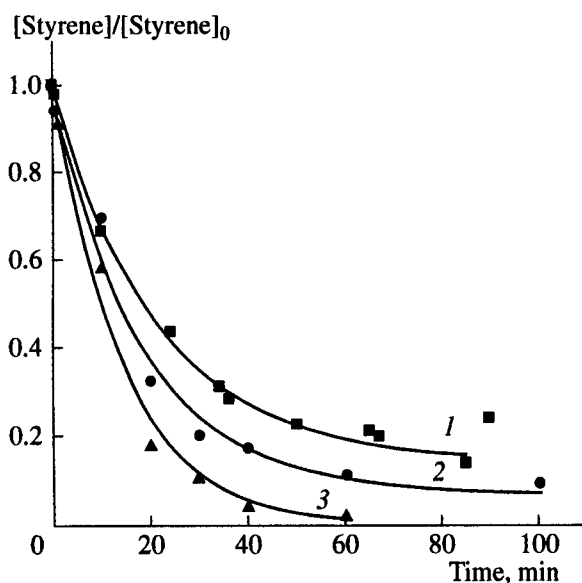
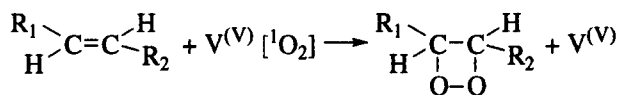


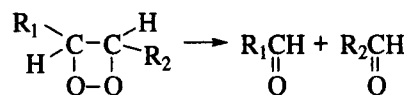
Fig. 6. The oxidation of styrene in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system ($[\text{V}^{(\text{V})}] = 10^{-3}$ mol/l, $[\text{styrene}]_0 = 5 \times 10^{-2}$ mol/l, and $[\text{H}_2\text{O}_2]_0 = 0.5$ mol/l) at 30°C (1) without additives and in the presence of BHT at a concentration of (2) 2.5×10^{-3} and (3) 1.3×10^{-2} mol/l.

The formation of I and the oxidative cleavage of the double bond $>\text{C}=\text{C}<$ in alkyl- and aryl-substituted alkenes can be explained in terms of the mechanism involving the formation of an intermediate $\text{V}^{(\text{V})}$ complex with singlet dioxygen as a ligand (reaction (I)).

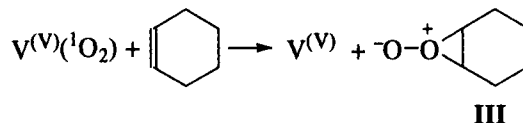
Depending on the substrate structure, the interaction of this complex (or free singlet dioxygen) with a substrate results in a compound of type I (reactions (IV) and (V)) or a corresponding dioxetane:



The decomposition of the intermediate dioxetane can result in the experimentally observed products:



The formation of dioxetanes on the reaction of alkenes with singlet dioxygen is an example of the cycloaddition following the Woodward–Hofmann rule. According to this rule, the reactivity of cyclohexene toward $({}^1\Delta_g)\text{O}_2$ should be low. Therefore, the reaction should be expected to occur via the Schenk intermediate (III):



We may assume that the products in allylic oxidation (III) are formed via this intermediate.

Thus, the above findings suggest that H_2O_2 decomposition (see Section 1.1) and the oxidation of unsaturated compounds in AcOH in the presence of vanadium complexes occur by a molecular rather than radical mechanism. The complex of vanadium(V) with O_2^- as a ligand probably does not participate in the oxidation of unsaturated organic substrates and H_2O_2 decomposition. All the data in hand point to ${}^1\text{O}_2$ or its complex with $\text{V}^{(\text{V})}$ formed in the reaction solution as the active oxidant in the system.

1.3. The oxidation of styrene and an unusual acceleration of the reaction by BHT. The consumption of styrene in the system, as well as H_2O_2 decomposition, shows an exponential dependence on time (Figs. 3 and 4). Even at a high concentration of BHT in the reaction mixture (up to 25% of the substrate amount), the shape of the styrene consumption curve remains the same; the induction period and inflection points are absent. This suggests a nonradical pathway for the oxidation of styrene in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system. Moreover, we found that the rate of styrene consumption increases with an increase in the BHT concentration (Fig. 6). This phenomenon, which is very unusual in the chemistry of oxidation processes, suggests that BHT is able

to increase the concentration of active oxidants (the $(^1\text{O}_2)\text{V}^{(\text{V})}$ complex or, possibly, dissolved $^1\text{O}_2$) in the solution.

BHT is an efficient radical trap [1]. Therefore, we can assume that BHT will react with the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ complex radical, the only detected radical in the course of H_2O_2 decomposition and the oxidation of organic substrates in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system. The above kinetic data suggest that this radical is not involved in the oxidation reactions. However, it seemed likely that the radical reacts with dissolved $^1\text{O}_2$, thus competing with the substrate for the active oxidant.

Indeed, peroxy radicals are efficient in quenching $^1\text{O}_2$. For example, the acylperoxy radicals $\text{CH}_3\text{COOO}^{\cdot}$, PhCOOO^{\cdot} , and $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOO}^{\cdot}$ quench the $^1\text{O}_2$ luminescence in benzene with a rate constant of $\sim 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$, which is close to the diffusion limit [19]. The peroxy radicals PhOO^{\cdot} , $t\text{-BuOO}^{\cdot}$, $\text{PhCH}_2\text{OO}^{\cdot}$, $\text{Ph}_2\text{CHOO}^{\cdot}$, and PhCOO^{\cdot} in benzene show the quenching with a rate constant of $(2\text{--}7) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ [20], which is close to the rate of quenching of $^1\text{O}_2$ by the superoxide radical anion in dimethyl sulfoxide ($1.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ [21]). Stable nitroxyl radicals also quench $^1\text{O}_2$, but at lower rates ($10^5\text{--}10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, for aliphatic radicals, and $10^6\text{--}10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ for aromatic radicals [22]). There is a good probability that the $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ complex radical will also transform singlet dioxygen to the triplet state.

Styrene can react with dissolved free $^1\text{O}_2$ in addition to its reaction with the $(^1\text{O}_2)\text{V}^{(\text{V})}$ complex. BHT is capable of decreasing the steady-state concentration of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radicals. If the rates of the $^1\text{O}_2$ interaction with **II** and the oxidation substrate are comparable, BHT may cause an increase in the steady-state concentration of $^1\text{O}_2$ (which is one of the oxidants) and in the rate of substrate oxidation.

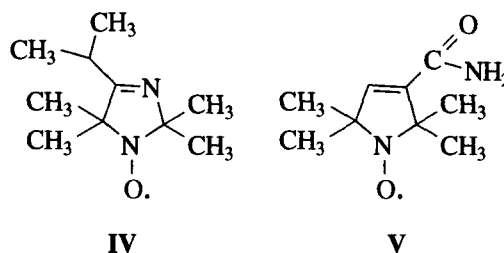
A comparison of Figs. 5 and 6 shows that BHT added in the same concentration does not accelerate the oxidation of 2-ethylanthracene. A possible reason is that the rate of the interaction of 2-ethylanthracene with $(^1\text{O}_2)\text{V}^{(\text{V})}$ is much higher than the rate of its interaction with dissolved free $^1\text{O}_2$. For example, 2-ethylanthracene suppresses the liberation of oxygen from the reaction solution, whereas styrene does not affect oxygen liberation. Therefore, within the framework of the proposed scheme, the quenching of $^1\text{O}_2$ on $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radicals in the presence of 2-ethylanthracene can be neglected.

Note that, in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system, BHT can also be oxidized to yield $^1\text{O}_2$ adducts. However, the fact that BHT does not decrease the rate of oxidation of sub-

strates (but sometimes increases this rate) suggests that, in the competition with other substrates for the active oxidant, BHT shows a lower accepting ability to $^1\text{O}_2$ in the reaction with the $(^1\text{O}_2)\text{V}^{(\text{V})}$ complex or dissolved $^1\text{O}_2$. On the other hand, the rate of BHT oxidation could be low because its concentration was at most 30% of the substrate concentration in all the experiments.

2. Abnormal Broadening of the ESR Spectra of Free Radicals in the Presence of $^1\text{O}_2$

To obtain additional data on the interaction of radicals with singlet dioxygen, we measured the ESR spectra of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ and stable nitroxyl radicals **IV** in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system, and **V** in the $\text{Mo(VI)}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system (pH 10.5) also generating $^1\text{O}_2$ [7].



The line width in the ESR spectra of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radicals depended on the conditions for H_2O_2 decomposition. For example, a narrow well-resolved octet was observed only if an inert gas (Ar or CO_2) was used to blow the reaction solution through (Fig. 2a, Table 3).

Purging the reaction solution with triplet dioxygen did not change the parameters of the spectrum—the g -factor and the hyperfine coupling constant (HCC)—but resulted in an increase in the line width by 1.2–1.5 G (Fig. 2b, Table 3). This phenomenon, which is called oxygen broadening, is due to spin–spin coupling between the radical and the paramagnetic $^3\text{O}_2$ molecule [23].

An abnormal broadening of the ESR signal of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ was observed without purging the reaction solution with gas, i.e., when gas reaction products were accumulated in the solution. In this case, the signal was so wide that the hyperfine structure was virtually absent (Fig. 2b, Table 3). The broadening observed (to $\sim 5.5\text{--}8.5 \text{ G}$) is much greater than that caused by the dipole–dipole interaction of $^3\text{O}_2$ and the radical, which is usually at most 1.5 G.

The spectral lines started to broaden a few minutes after the Ar flow was stopped and narrowed again once the gas flow was resumed. This suggests that abnormal broadening of the ESR line could be due to a highly volatile product accumulated during H_2O_2 decomposition in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ system. However, our experiments showed that volatile products, such as CO_2 , CH_3OH , and CH_3OOAc , did not affect the line width in ESR spectra. All of our findings suggest

Table 3. Parameters of ESR spectra of the $V^{(V)}(O_2^{\cdot-})$ complex radical in the $H_2O_2/V^{(V)}/AcOH$ catalytic system ($[V^{(V)}] = 10^{-2}$ mol/l, $[H_2O_2]_0 = 1$ mol/l, and $[H_2O]_0 = 2.3$ mol/l; $20^\circ C$)

Flowing gas	Time*, min	$g \pm 0.0003$	$(\alpha_V \pm 0.2) \times 10^{-4}, cm^{-1}$	$\alpha_V \pm 0.2^{**}, G$	Error***
Ar	12.0	2.0112	4.5	2.3	0.014
	18.8	2.0112	4.5	2.2	0.017
	40.0	2.0112	4.5	2.3	0.024
	72.0	2.0112	4.5	2.2	0.021
O ₂	16.5	2.0112	4.5	3.9	0.019
	22.0	2.0112	4.5	4.0	0.017
	33.0	2.0112	4.5	4.1	0.017
	46.5	2.0112	4.5	3.8	0.020
	54.8	2.0112	4.5	3.9	0.017
Without gas flow	3.5	2.0111	4.5	6.9	0.014
	8.5	2.0110	4.7	6.9	0.014
	35.0	2.0109	4.7	6.2	0.014
	48.0	2.0109	4.6	7.5	0.012
	67.0	2.0109	4.6	7.3	0.012

* Time elapsed after the addition of H_2O_2 to the catalyst solution.

** The spectra were treated on a computer using the software published in [24]. Within the framework of the model used, the broadening parameters were approximated by the equation $\Delta H = \alpha + \beta m_1 + \gamma m_1^2$, where m_1 is the projection of the nuclear spin along the external magnetic field, and α is the homogeneous broadening parameter identical for all lines of the hyperfine structure. βm_1 and γm_1^2 values were found to be two orders of magnitude lower than α and not included.

*** The standard deviation.

that broadening was due to singlet dioxygen formed by H_2O_2 decomposition in the $V^{(V)}/H_2O_2/AcOH$ system.

Analogous abnormal broadening was found in the ESR spectra of other radicals in the catalytic systems capable of generating 1O_2 . For example, a change in the ESR spectrum of the stable nitroxyl radical IV measured during hydrogen peroxide decomposition in the $V^{(V)}/H_2O_2/AcOH$ system is analogous: the superposition of two well-resolved signals (an octet assigned to $V^{(V)}(O_2^{\cdot-})$ and a triplet of the radical IV) was observed only if argon purged the solution (Fig. 7a). Five minutes after purging was stopped, the lines of both radicals broadened to ~ 10 G (Fig. 7b) and restored their original widths once the Ar flow was resumed (Fig. 7c). These variations in the line widths are observed only if H_2O_2 and the radical IV are present in the solution. The rate of radical consumption in the system (Fig. 8) was low enough for recording several ESR spectra. Recall that the radical II was present at a steady-state concentration, which decreased as H_2O_2 was consumed.

We recorded the ESR spectrum of the nitroxyl radical V in the $Mo(VI)/H_2O_2/H_2O$ catalytic system (pH 10.5), which is known as capable of generating 1O_2 with almost 100% yield [7, 24]. In this system, radical V was virtually not consumed (Fig. 8). The line

width in the ESR spectra changed as for the $V^{(V)}/H_2O_2/AcOH$ system. For example, with Ar purging, radical V (10^{-4} mol/l) in the $Mo(VI)/H_2O_2/H_2O$ system ($[MoO_4^{2-}] = 10^{-2}$ M, $[H_2O_2]_0 = 1$ M, pH 10.5) gave a narrow well-resolved triplet with $g = 2.0049$, $a_V = 15.49$ G, and a line width of 1.52 G (Fig. 9a). With 3O_2 instead of Ar, the line broadened to 2.50 G due to the dipole-dipole interaction (Fig. 9b). Without purging the reaction solution during H_2O_2 decomposition, the line was as wide as 8.3 G (Fig. 9c). Once purging resumed, the ESR line narrowed again. Such narrowing and broadening of the spectral line, depending on whether the Ar flow was on or off, could be observed many times until H_2O_2 completely decomposed.

The spectral parameters (g -factor, hyperfine coupling constant, and integral intensity) of all the investigated radicals did not depend on the nature of the gas dissolved in the reaction mixture. This fact suggests that, in each specific case, the signal, be it wide or narrow, corresponded to the same radical.

Thus, the ESR spectra of such different radicals as $V^{(V)}(O_2^{\cdot-})$ and nitroxyl radicals IV and V in the quite different catalytic systems (different metal catalysts and acidic and alkaline media) had common features: broadening by 5–8 G in the absence of Ar and narrow-

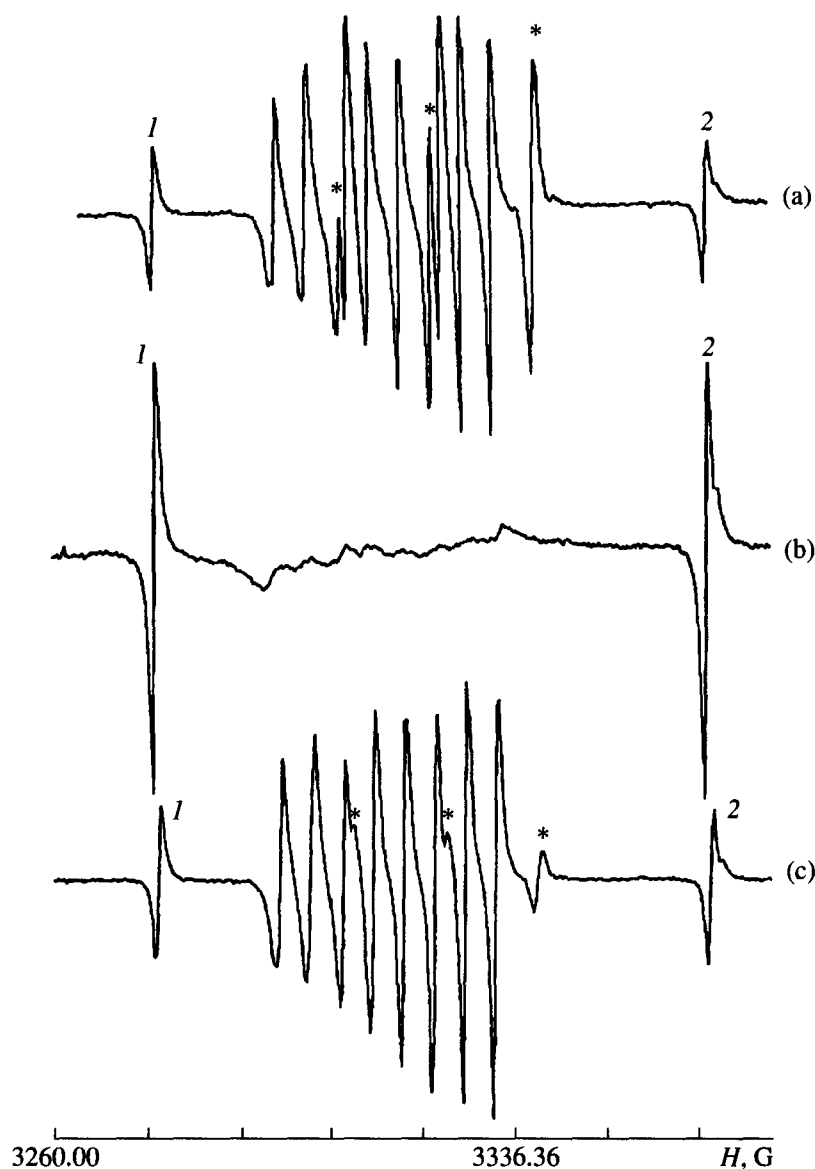


Fig. 7. The superpositions of the ESR signals from radical IV and $V^{(V)}(O_2^{\cdot-})$ in the $V^{(V)}/H_2O_2/AcOH$ system ($[V^{(V)}] = 10^{-2}$ mol/l, $[H_2O_2]_0 = 1$ mol/l, and $[IV] = 2 \times 10^{-5}$ mol/l) at $20^\circ C$ (a) upon Ar blowing, (b) without blowing, and (c) once the Ar blowing was restarted. Components of the triplet corresponding to radical IV are asterisked; the (1) third and (2) fourth components of the ESR signal from Mn^{2+}/MgO used as an internal standard.

ing with the Ar purging of the reaction solution. This suggests that the reason for anomalous broadening is common for these systems. A common property of these catalytic systems is their ability of generating 1O_2 by hydrogen peroxide decomposition.

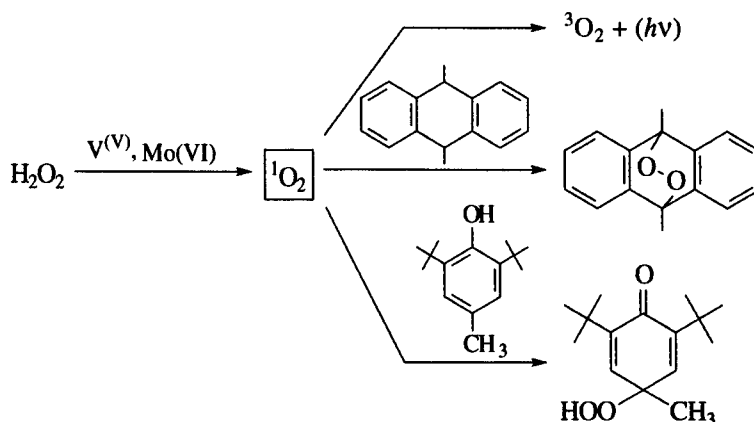
It is possible that, in both the catalytic systems, singlet dioxygen is rapidly quenched by the solvent (both water and AcOH are efficient quenchers), which results in a high (higher than the solubility limit) concentration of triplet dioxygen in the solution. Molin and Ermolaev [25] hypothesized that, in such supersaturated 3O_2 solutions, the relaxation time of protons may decrease. To test our conjectures on the mechanism, we recorded the

ESR spectra of nitroso radical V in a hydrogen peroxide aqueous solution containing $FeSO_4$, which is known as incapable of 1O_2 generating [7]. The rate of H_2O_2 decomposition was the same as in the experiments with Mo(VI). It was found that, during hydrogen peroxide decomposition, the ESR signal of radical V broadened only to 2.7–3.0 G (Fig. 10b), which is typical of the paramagnetic broadening of ESR lines in solutions saturated with triplet dioxygen.

Thus, the reason for the anomalous broadening (to 7–10 G) of the ESR line of oxygen-centered radicals is their interaction with 1O_2 .

With a continuous flow of an inert gas, the steady-state concentration of dissolved $^1\text{O}_2$ decreases; the result is the narrowing of the spectral lines of the radicals. However, the steady-state concentration of $^1\text{O}_2$

can also be decreased by the addition of a singlet dioxygen trap to the solution. For example, anthracenes and BHT react with singlet dioxygen to yield the corresponding products:

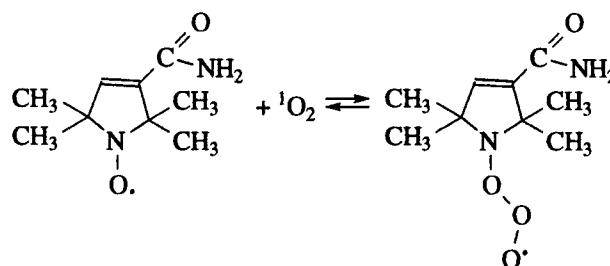


Indeed, in the presence of, for example, BHT, the ESR spectrum of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ radicals presented a well-resolved octet (Fig. 11a). Once BHT was exhausted, the fine structure of the spectrum disappeared because of its anomalous broadening (Fig. 11c). Of special interest is Fig. 11b, demonstrating the broadening of the ESR spectrum of $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$ during the consumption of BHT.

Unlike triplet dioxygen, $^1\text{O}_2$ molecules are diamagnetic and cannot interact with a paramagnetic species by the dipole-dipole mechanism. At the same time, it is known that peroxy radicals are efficient in quenching

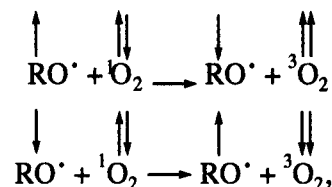
$^1\text{O}_2$ (see above). Therefore, it can be assumed that the anomalous broadening of the ESR line of a radical in the presence of singlet dioxygen is the result of their interaction during the process of $^1\text{O}_2$ quenching.

The mechanism of this interaction is still unclear. It can involve a reversible addition of the radical to $^1\text{O}_2$, for example, by the reaction



This equilibrium could give rise to the broadening of the ESR line of the radical. In this case, the equilibrium constant and, consequently, the broadening should depend on the concentrations of reactants. However, our experiments showed that this is not the case (Fig. 12): in the range between 10^{-2} and 5×10^{-2} mol/l of the catalyst concentration and between 10^{-4} and 10^{-3} mol/l of radical V concentration, the maximal broadening of the ESR line in the experiments is virtually the same and changes at the same rate during the run.

It is also possible that radicals catalyze the quenching of singlet dioxygen:



where RO^{\cdot} is an oxygen-centered radical (IV, V, or $\text{V}^{(\text{V})}(\text{O}_2^{\cdot-})$). This reaction can involve the spin-spin

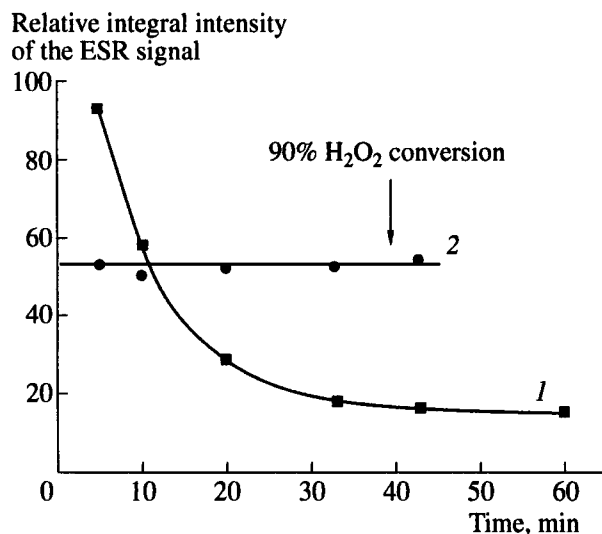


Fig. 8. The relative integral intensity of the ESR signal vs. time curves for radicals (1) IV and (2) V measured during H_2O_2 decomposition in the $\text{V}^{(\text{V})}/\text{H}_2\text{O}_2/\text{AcOH}$ and $\text{Mo(VI)}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ systems, respectively: (1) $[\text{V}^{(\text{V})}] = 10^{-2}$ mol/l, $[\text{H}_2\text{O}_2]_0 = 1$ mol/l, $[\text{IV}] = 2 \times 10^{-5}$ mol/l, Ar, $T = 20^\circ\text{C}$; (2) $[\text{Mo(VI)}] = 2 \times 10^{-2}$ mol/l, $[\text{H}_2\text{O}_2]_0 = 0.2$ mol/l, $[\text{V}] = 2 \times 10^{-5}$ mol/l, a phosphate buffer with pH 10, $T = 20^\circ\text{C}$.

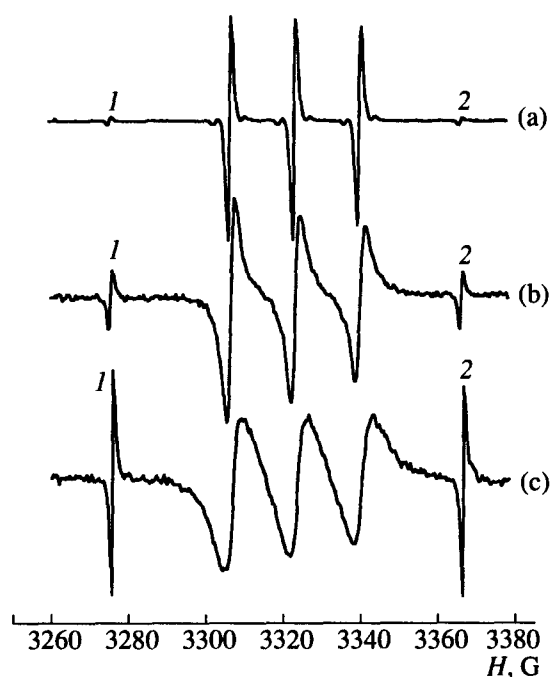


Fig. 9. The ESR spectra of radical V in the Mo(VI)/H₂O₂/H₂O system ([Mo(VI)] = 10⁻² mol/l, [H₂O₂]₀ = 0.2 mol/l, [V] = 2 × 10⁻⁵ mol/l, a phosphate buffer with pH 10) measured at 20°C upon (a) Ar and (b) O₂ blowing and (c) without blowing; the (1) third and (2) fourth components of the ESR signal from Mn²⁺/MgO used as an internal standard.

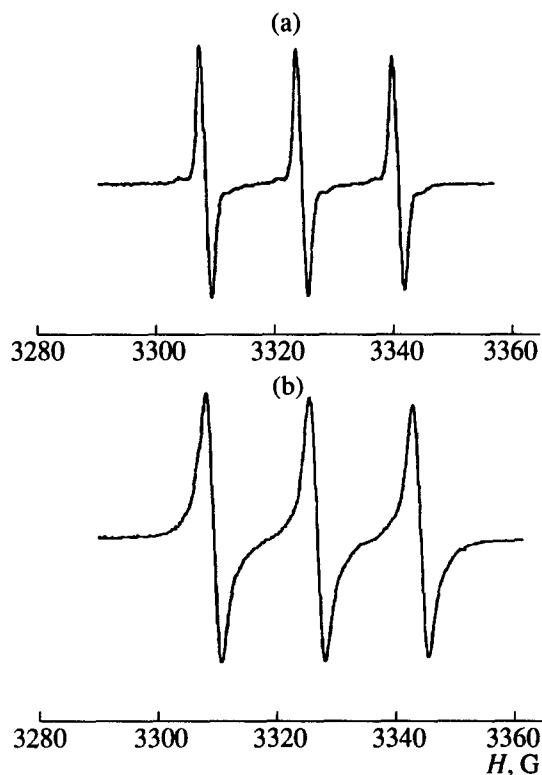


Fig. 10. The ESR spectra of radical V in the Fe(II)/Fe(III)/H₂O₂/H₂O system ([Fe(II)] = 10⁻² mol/l, [H₂O₂]₀ = 0.2 mol/l, [V] = 10⁻⁴ mol/l, pH 10, T = 20°C) measured (a) before the addition of H₂O₂ and (b) during H₂O₂ decomposition without inert gas blowing.

interaction or electron exchange. To confirm or disprove this mechanism, we should obtain additional quantitative data, in particular, on the lifetime and steady-state concentration of ¹O₂ in the above systems. Currently, the mechanistic studies of the phenomenon are underway.

In conclusion, we note that the phenomenon discovered in the chemistry of singlet dioxygen—the anomalous (to 10 G) broadening of ESR lines of radicals due to their interaction with dissolved ¹O₂—can be used as a probe for ¹O₂ in a solution, because even low (below 10⁻⁷ mol/l) concentrations of singlet dioxygen noticeably broaden the ESR line.

This work and other recent studies show that hydrogen peroxide can be used as a source of singlet dioxygen formed via a nonradical pathway under the action of metal complex catalysts [6–11]. The list of such catalysts possibly goes far beyond the scope of known examples and even involves components of biologically important objects, such as the oxygen-generating complex of chloroplasts of higher plants [26]. However, the formation of ¹O₂ in a cell would lead to its destruction. It is not improbable that the quenching of ¹O₂ on paramagnetic centers, such as manganese, iron, nickel, and other complexes [27], is one of the ways to protect biosystems against the destructive action of ¹O₂. In this context, the problem of the interaction of singlet

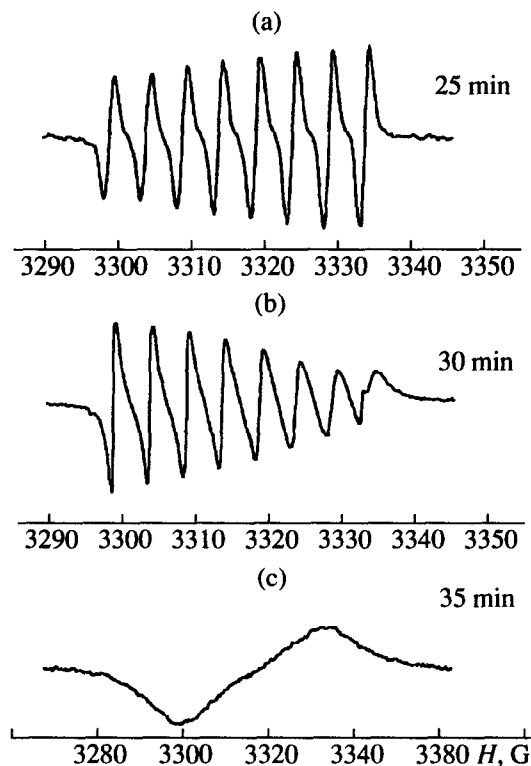


Fig. 11. The ESR spectra of V(V)(O₂⁻) in the V(V)/H₂O₂/AcOH system in the presence of BHT ([V(V)] = 10⁻² mol/l, [H₂O₂]₀ = 1 mol/l, [BHT] = 0.123 mol/l, T = 20°C) (a) before BHT consumption, (b) during the consumption of BHT, and (c) once BHT was exhausted.

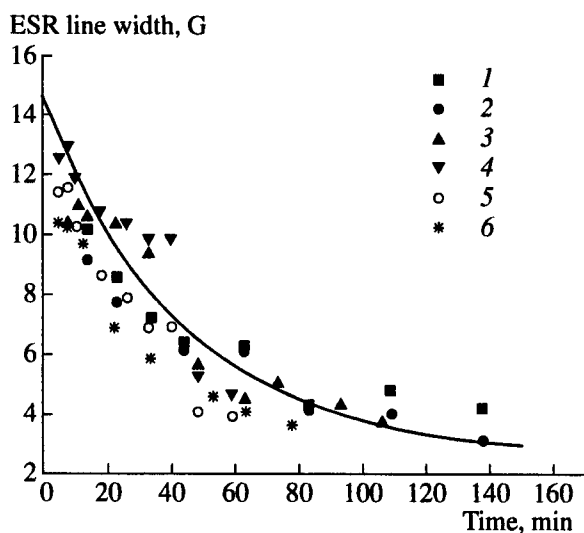


Fig. 12. The narrowing of the ESR line of radical V during H_2O_2 decomposition in the $\text{Mo(VI)}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system ($[\text{H}_2\text{O}_2]_0 = 0.2 \text{ mol/l}$, a phosphate buffer with pH 10, Ar, $T = 20^\circ\text{C}$) at $[\text{Mo(VI)}] = 10^{-2} \text{ mol/l}$ and $[\text{V}]$ (1) 5×10^{-3} , (2) 10^{-3} , and (3) 10^{-4} mol/l and also at $[\text{V}] = 10^{-4} \text{ mol/l}$ and $[\text{Mo(VI)}]$ (4) 10^{-2} and (5) $5 \times 10^{-2} \text{ mol/l}$; (6) in the presence of NaN_3 (10^{-3} mol/l).

dioxygen with paramagnetic centers can also be essential for studying the reactions forming the basis of biological processes.

ACKNOWLEDGMENTS

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