

Pathways of $^1\text{O}_2$ transfer in the oxidation of anthracenes with the $\text{H}_2\text{O}_2/\text{V}^{\text{V}}/\text{AcOH}$ system

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Dedicated to Professor Helmuth Knözinger in recognition of his outstanding contribution into catalytic science.

Abstract

Anthracene and its alkyl derivatives were found to undergo oxidation by the $\text{V}^{\text{V}}/\text{H}_2\text{O}_2/\text{AcOH}$ catalytic system via a polar mechanism involving the transfer of singlet dioxygen from the vanadium(V)/ $^1\text{O}_2$ exñplex to the molecule of unsaturated substrate. The free singlet dioxygen $^1\text{O}_2(^1\Delta_g)$ molecule is practically inactive toward anthracene in the AcOH solution. The vanadium(V) complex with the singlet dioxygen ligand was suggested to be the only oxidant species active in the reaction. The deactivation rate of the complex is ~ 1.5 times less than the rate of its reaction with 2-ethylanthracene (10^{-2} M). Meantime, the analogous ratio of the $^1\text{O}_2$ dissolved in AcOH solution is ~ 15 at the same 2-ethylanthracene concentration. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen peroxide decomposition; Homogeneous catalysis; Singlet dioxygen formation; Vanadium(V) complexes; Kinetic of anthracenes oxidation; Singlet dioxygen transfer to substrate molecule

1. Introduction

Hydroperoxides are known as the oxidants for aromatic hydrocarbons in the presence of transition metal compounds since the Fenton discovery [1]. The catalysts containing metal atoms with at least two accessible oxidation states, for example Fe(I)-Fe(II)-Fe(IV)-Fe(V), have been studied in detail [2]. The reactivity of hydroperoxides and their metal complexes is known to be sensitive to the nature of solvent, metal ion and ligand [3–5]. In the case of

complexes of metals with d^0 non-bonding configuration, molecular pathways of H_2O_2 activation are possible [6–11].

Hydrogen peroxide decomposition to form triplet dioxygen and water is a thermodynamically favourable process (see Table 1) and is catalyzed by a number of metals, such as Fe, Co, Cu, etc. (see Eq. (1)).



H_2O_2 decomposition to form singlet dioxygen, though being thermodynamically less favoured, (see Table 1) is also known to proceed in the presence of

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Table 1
Thermodynamics of H₂O₂ decomposition

Product of H ₂ O ₂ decomposition	ΔG_{298}^0 kcal/mol
³ O ₂	-56
¹ O ₂	-24
O ₃	-45

Ca(OH)₂, H₂TiO₃, NaVO₃, Na₂MoO₄, Na₂WO₄, etc. in alkaline media [12] and V^V complexes in AcOH solution [6–11,13–15] (see Eq. (2)).



Ozone formation from H₂O₂ is also a thermodynamically favourable reaction (see Table 1). The fact that a small amount of ozone forms during the stoichiometric decomposition of various peroxides by concentrated H₂SO₄ has been known for about 100 years [16]. Peroxo compounds of U, Mo, B, Ti, V, Caro's acid, peroxycarboxylic acid and their salts decompose in concentrated sulfuric acid to form stoichiometric amounts of dioxygen and traces of ozone [17]. In contrast to this, the catalytic formation of ozone in the course of hydrogen peroxide decomposition has been observed during H₂O₂ decomposition in CH₃COOH and, especially, in a CF₃COOH solution containing vanadium(V) compounds [7,18] (see Eq. (3)).



Perfluoralkenes [11,19,20] and perfluorarenes [11,21], which are usually resistant toward oxidation, readily

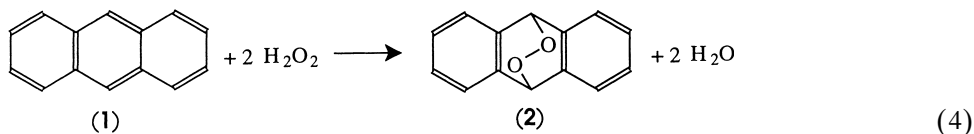
undergo oxidation in the V^V/H₂O₂/CF₃COOH system.

A number of oxidation reactions with H₂O₂ catalyzed by V^V complexes in carboxylic acid solution has been studied [6–11,13–15]. It was found that one-electron reduction of V^V by H₂O₂ does not occur in these solutions. In neutral or acid aqueous solutions, the interaction of H₂O₂ with V^V gives rise to the formation of stable peroxo complexes of the [V(O₂)_nO_m]^{5-2(n+m)+} type where *m*, *n* = 1, 2. The complexes are quite stable in aqueous solution at ambient temperature [22,23]. In contrast to aqueous solutions, the decomposition of H₂O₂ and AcOOH [24] is catalyzed with vanadium(V) compounds in AcOH solution.

The highly selective oxidation of alkenes into corresponding aldehydes [11], 2-ethylanthracene (EA) into 2-ethylanthraquinone (EAQ) [13,14] and cyclohexane into cyclohexanol and cyclohexanon [8] have been observed in the system under question.

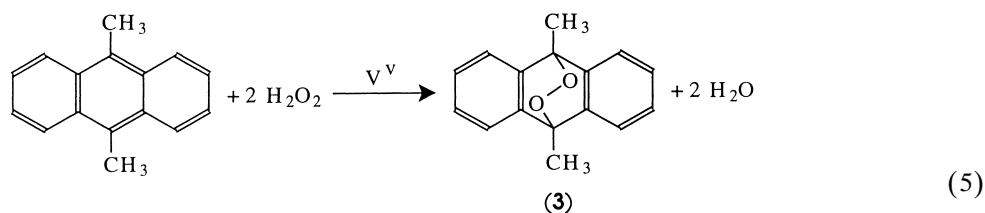
Preliminary data available suggest that singlet dioxygen is involved into the anthracene oxidation. The 100% yield of anthraquinone can be achieved by the oxidation of anthracene (1) with H₂O₂ in an AcOH solution containing V^V complexes. Anthrone, bianthrone or anthracene radical cation were not detected under the conditions of anthracene oxidation in the V^V/H₂O₂/AcOH system. These facts imply the reactive species of the system not to be capable of one-electron oxidation of the substrate molecules.

Based on the ¹H NMR spectroscopy and GC-MS data, the endoperoxide 9,10-dihydro-9,10-epidioxy anthracene (2) has been found to be the first observed product of the oxidation under these conditions [10,13] (see Eq. (4)).



Endoperoxide 2 is unstable and undergoes further transformations to give anthraquinone as the final product [25]. More direct evidence for this mecha-

nism was obtained by studying the oxidation of 9,10-dimethylanthracene in the H₂O₂/V^V/AcOH system [7,10,11], as depicted by Eq. (5).



The reaction yields $\sim 90\%$ of yellow crystalline product at 20°C in ~ 1 h, which was characterised by the elemental analysis, ^1H NMR and GC-MS data [11]. The NMR data and finding of the peroxy group in the reaction product gave evidence for the efficient oxidation of 9,10-dimethylanthracene to 9,10-dimethyl-9,10-epidioxy anthracene (**3**) (Eq. (5)). The formation of endoperoxides is one of the test reactions indicating the involvement of singlet dioxygen molecules into oxidative processes [26].

The formation of **2** and **3** can be rationalised assuming a mechanistic scheme involving the intermediate formation of a vanadium(V) complex, which contains singlet dioxygen as a ligand,¹ followed by the interaction of this complex with a substrate molecule affording **2** and **3** molecules (see Scheme 1, route **a**). Another possibility is that the active oxidant is a free singlet dioxygen molecule dissolved in the reaction solution (see Scheme 1, route **b**).

The fact that V^{V} compounds catalyze H_2O_2 decomposition in AcOH solution giving rise to $^1\text{O}_2$ in high yield was directly confirmed in works [27–30]. The formation of $^1\text{O}_2$ was detected by both chemical reactions and characteristic chemiluminescence at 1275 nm. Based on our phosphorescence study, the life-time of $^1\text{O}_2$ generated photochemically by hematoporphyrine photosensitization is equal to $23 \pm 1 \mu\text{s}$ in AcOH solution at room temperature [30]. Correspondingly, the maximum concentration of $^1\text{O}_2$ achieved at $[\text{H}_2\text{O}_2]_{\text{init}} = 1 \text{ M}$ in catalytic experiments was at most $\sim 3 \times 10^{-9} \text{ M}$.

Another species responsible for anthracene oxidation is assumed to be a complex with an $^1\text{O}_2$ molecule as a ligand of composition $[(\text{O}_2^{2-})_{n-2}\text{V}^{\text{V}}(^1\text{O}_2)]$ ($n =$

2 or 3) (see Scheme 1). To evaluate the contribution of the two routes (**a** and **b** in Scheme 1) we studied the kinetics of EA oxidation in the $\text{H}_2\text{O}_2/\text{V}^{\text{V}}/\text{AcOH}$ system

2. Experimental

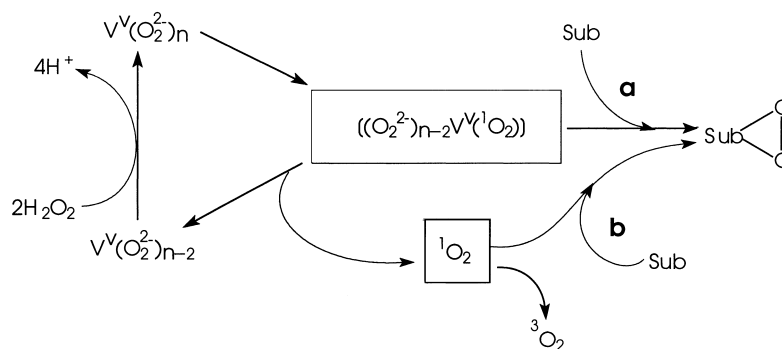
2.1. Materials

Glacial acetic acid and hydrogen peroxide (9.67 M aqueous solution), both of analytical grade, were used without additional purification. Concentrated solutions of H_2O_2 (17.8 M) were prepared by distillation of commercial H_2O_2 (analytical grade). Anthracene, 9-methylanthracene, 9-phenylanthracene, 9,10-dimethylanthracene *trans*-1,2-diphenylethylene, 1,1-diphenylethylene (all at least of 95% purity by GC analysis), and NH_4VO_3 (analytical grade) were used as received. α -Methylstyrene (of reagent grade) was purified by distillation before the experimental runs and controlled by GC analysis. Commercial $\text{VO}(\text{acac})_2$ was purified by recrystallization from chloroform.

2.2. Preparation of catalyst solutions

To prepare an AcOH solution containing V^{V} , 100 mg of finely ground NH_4VO_3 was refluxed in 100 ml of AcOH during 4–5 h. The undissolved NH_4VO_3 was filtered off. ICP-MS spectra of solutions diluted by water were recorded on an ICP-MS HP 4500 instrument (Acq. mode: spectrum, NH_4VO_3 aqueous solution as external standard). Based on ICP-MS analysis, the concentration of V^{V} in the solution obtained was equal to $3.7 \times 10^{-3} \text{ M}$. The solutions prepared in this way were used mainly in the ESR and NMR experiments and also for kinetic runs. In some kinetic experiments $\text{VO}(\text{acac})_2$, which

¹ No data available concerning the coordination sphere composition except for $^1\text{O}_2$ and O_2^{2-} ligand presence in the complexes. Hence all other ligands are omitted from the formulae.



Scheme 1. Possible pathways for anthracene (sub)oxidation with the $\text{H}_2\text{O}_2/\text{V}^{\text{V}}/\text{AcOH}$ system.

is well soluble in AcOH was used as the starting compound. ESR spectra showed the VIV signal of $\text{VO}(\text{acac})_2$ to disappear after the first H_2O_2 portions added to the V^{V} compound solution. When $\text{VO}(\text{acac})_2$ was used instead of NH_4VO_3 , no change in the composition of the reaction products and on the reaction rates was found.

2.3. H_2O_2 decomposition

Hydrogen peroxide decomposition was studied using a double-jacketed Pyrex reaction vessel equipped with a reflux condenser, dropping funnel and magnetic stirrer at 30°C . In a typical experiment, 2.4 ml (42.5 mmol) of aqueous (9.67 M) H_2O_2 was added to a solution of 1.33 mg (0.005 mmol) of $\text{VO}(\text{acac})_2$ in 50 ml of AcOH. The H_2O_2 consumption was followed by iodometry.

2.4. Oxidation procedure and analyses of reaction products

The competitive oxidation of *trans*-1,2-diphenylethylene, 1,1-diphenylethylene, α -methylstyrene, anthracene and its derivatives was carried out at 30°C in a jacketed temperature-controlled glass reaction vessel equipped with a magnetic stirrer. In a typical experiment, 90 μl (1.6 mmol) of aqueous (17.8 M) H_2O_2 was added to a solution of 7.55 mg (0.0285 mmol) of $\text{VO}(\text{acac})_2$, 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 AcOH. Hydrogen peroxide was completely exhausted in 2 h after starting the experiment. After this period of time, concentrations of the unreacted substrates were determined by GLC. The ratio of the rate constant for the substrate reaction to that for anthracene was calculated by the formula [31]:

$$\frac{k_i}{k_a} = \frac{\ln(S_i/[S_i]_0)}{\ln(S_a/[S_a]_0)}$$

where $[S_i]$ and $[S_i]_0$ are the final and initial concentrations of substrate S_i , $[S_a]$ and $[S_a]_0$ are the final and initial concentrations of anthracene. Average values of three runs are shown in Table 2.

EA oxidation was carried out at 34.5°C in a jacketed temperature-controlled glass reaction vessel equipped with a magnetic stirrer. In a typical experiment, 96.6 μl (1.72 mmol) of aqueous (17.8 M) H_2O_2 was added to a solution of 2.10 mg (7.93 $\times 10^{-3}$ mmol) of $\text{VO}(\text{acac})_2$ and 58.5 mg (0.284 mmol) of 2-ethylanthracene in 14.2 ml of glacial AcOH. Reaction solution was sampled (0.5 ml) in 2, 4, 6, 8, 12 and 25 min. The H_2O_2 consumption was followed by iodometry. The concentration of substrate was determined by GLC.

Analysis of *trans*-1,2-diphenylethylene, 1,1-diphenylethylene, α -methylstyrene, anthracene: A solution of dodecane (internal GLC standard, 10^{-2} M) in benzene (0.5 ml) was added to 0.5 ml of the reaction mixture. Then 5 ml of water was added, the organic layer was separated and washed with 1 ml of 5% aqueous sodium carbonate. GLC analysis was carried out with a 3700 GLC instrument (Russia)

Table 2

Oxidation of alkenes and anthracenes by H₂O₂ catalyzed with V^V compounds in AcOH solution at 30°C and by free dissolved ¹O₂

Substrate	$k_{\text{substr}}/k_{\text{anthr}}$ measured	$k_{\text{substr}}/k_{\text{anthr}}$ calculated for free ¹ O ₂ based on data [32]
α-Methylstyrene	0.464 ± 0.005	Not determined ^a
1,1-diphenylethylene	0.68 ± 0.01	Not determined ^a
Trans-1,2-diphenylethylene	0.145 ± 0.009	Not determined ^a
Anthracene	1	1
9-Methylanthracene	1.15 ± 0.05	21
9,10-dimethylanthracene	15 ± 3	140
9-Phenylanthracene	1.13 ± 0.08	2.8

^a The rate of reaction between free ¹O₂ and these substrates is of 2–3 order of magnitudes less than that of free ¹O₂ quenching by the solvent. Thus, the rates of reaction between these substrates and free dissolved ¹O₂ cannot be determined with competitive reactions approach.

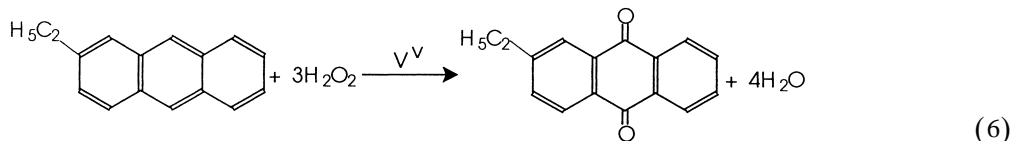
(capillary column, 0.2 mm × 25 m, with 0.33 μm HP-1, FID), and an integrator ITs-26 (Bulgaria). $T_{\text{inj}} = 250^\circ\text{C}$, $T_{\text{col}} = 120^\circ\text{C}$, delay 2 min, $10^\circ\text{C}/\text{min}$, 200°C , delay 2 min, $P = 1$ bar, split ratio 1/40.

Sampling of anthracene, 2-ethylanthracene, 9-methylanthracene, 9,10-dimethylanthracene and 9-phenylanthracene was carried out as mentioned above, using 0.5 ml of a 10^{-2} M solution of hexadecane in benzene. GLC analysis: $T_{\text{inj}} = 270^\circ\text{C}$, $T_{\text{ini}} = 200^\circ\text{C}$, delay 2 min, $10^\circ\text{C}/\text{min}$, 270°C , delay 2 min, $P = 1.5$ bar, split ratio 1/40.

The experimental data were processed using the ORIGIN 5.0 program.

3. Results and discussion

EAQ was found to be the main oxidation product (yield 60–90%) in the V^V/H₂O₂/AcOH catalytic system in the conditions of kinetic experiments (see Eq. (6))



2-Acetylanthraquinone (2–7%) was found as the side reaction product. Another possible intermediate, 2-ethylanthrone, which can point to free-radical reaction pathways was not found by both GLC and spectral techniques.

Under the assumption that ¹O₂(¹Δ_g) is the active oxidant species in the V^V/H₂O₂/AcOH system (Scheme 1, route **b**) and the yield of ¹O₂ is close to 100%, the following relation (see Eq. (7)) should be expected to describe the consumption of hydrogen peroxide and EA:

$$\frac{d[\text{H}_2\text{O}_2]}{d[\text{S}]} = 2 \frac{k_d + k_s[\text{S}]}{k_s[\text{S}]} \quad (7)$$

where [S] is the substrate concentration, $k_d = 4.4 \times 10^4 \text{ s}^{-1}$ is the quenching constant of ¹O₂ in AcOH, $k_s = 3 \times 10^5 \text{ M s}^{-1}$ is the constant of the interaction

of ¹O₂ with the EA molecule as measured in independent experiment at 25°C [29,30].

Integration of Eq. (7) with account of complete consumption of hydrogen peroxide after a long reaction time ($[\text{H}_2\text{O}_2]_\infty \approx 0$), gives the Eq. (8):

$$\frac{(\text{H}_2\text{O}_2)_0}{S_0} = 2 \left(\eta_\infty - \frac{k_d}{k_s S_0} \ln(1 - \eta_\infty) \right) \quad (8)$$

where $[\text{H}_2\text{O}_2]_0$ and $[S]_0$ are the initial concentrations of H₂O₂, substrate and $[S]_0$ is the substrate concentration after H₂O₂ has been exhausted. Correspondingly, $\eta_\infty = ([S]_0 - [S]_\infty)/[S]_0 = 1 - ([S]_\infty/[S]_0)$ is the limiting substrate conversion achieved after complete consumption of H₂O₂.

In a particular case where the EA initial concentration $[S]_0 = 8.45 \times 10^{-3} \text{ M}$ and $([S]_\infty/[S]_0) = e$, the substrate conversion $\eta_\infty \approx 0.63$ should be achieved

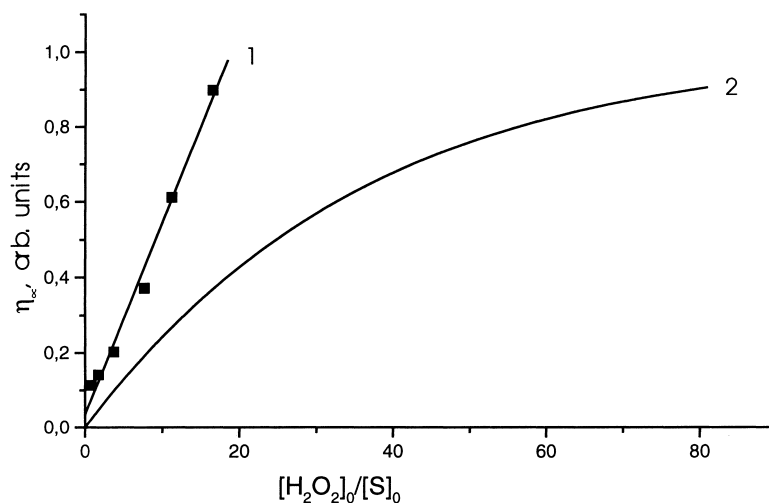


Fig. 1. The limiting EA conversion (η_∞) vs. the ratio ($[H_2O_2]_0/[S]_0$) plot: (1) experimental curve, conditions: $[S]_0 = 8.45 \times 10^{-3}$ M, $[V] = 3.61 \times 10^{-3}$ M, 30°C; (2) curve calculated according to Eq. (7) under assumption that free dissolved 1O_2 is the active oxidant.

when the ratio ($[H_2O_2]_0/[S]_0$) = 36. It can be seen from the experimental dependence of EA conversion on the ($[H_2O_2]_0/[S]_0$) ratio (Fig. 1) that the $\eta_\infty \approx 0.63$ conversion is in fact achieved at the substantially less value of ($[H_2O_2]_0/[S]_0$) = 11.7.

Moreover, the experimental points on the plot for the EA limiting conversion (η_∞) versus ($[H_2O_2]_0/[S]_0$) ratio well fit to a straight line. Meanwhile, the curve calculated by Eq. (7) should increase monotonously and asymptotically approach unity, if

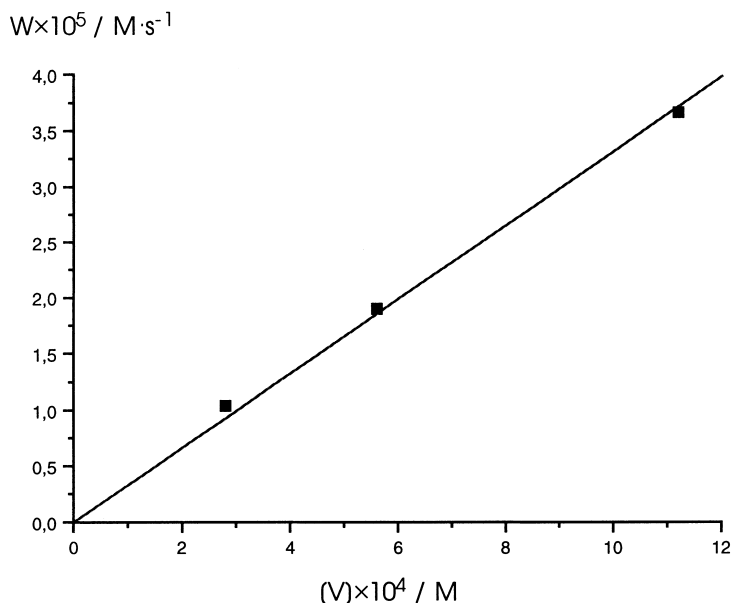


Fig. 2. EA oxidation rates (W) vs. catalyst concentration ($[V]$) plot. Conditions: $[S]_0 = 6.0 \times 10^{-3}$ M, $[H_2O_2]_0 = 0.144$ M, 34.5°C.

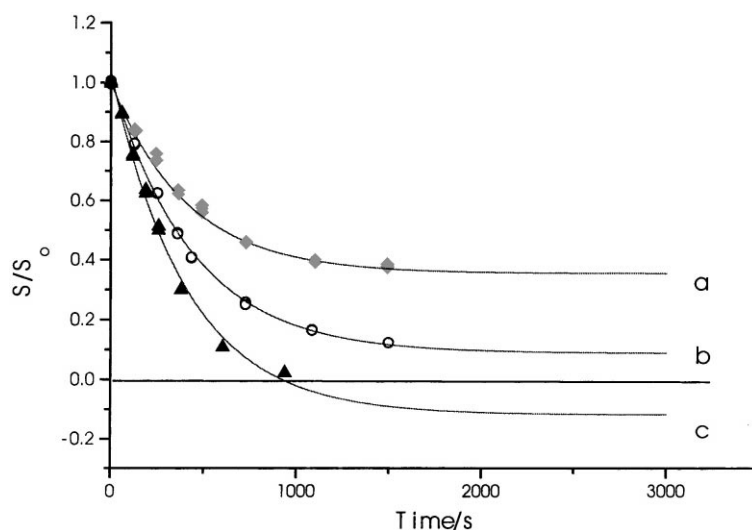


Fig. 3. The kinetic curves for EA conversion (S/S_0) at different initial concentrations of hydrogen peroxide ($[H_2O_2]_0$). Conditions: $[V] = 5.6 \times 10^{-4}$ M, 34.5°C . (a) $[S]_0 = 0.0208$ M, $[H_2O_2]_0 = 0.082$ M; (b) $[S]_0 = 0.0202$ M, $[H_2O_2]_0 = 0.123$ M; (c) $[S]_0 = 0.0208$ M, $[H_2O_2]_0 = 0.204$ M.

dissolved 1O_2 has played the role of the active oxidant (Fig. 1). These data suggest free dissolved singlet dioxygen not to be the only oxidant in the system under study.

The competitive oxidation in pairs of anthracene and alkyl substituted anthracenes was studied (see Table 2). The value of the rate constants ratios was found to be independent of the conversion degrees.

Table 3
The parameters of Eq. (9)^a

$[S]_0$, M	$[H_2O_2]_0$, M	$1/k_{ef}$	A_1	y_0
0.0508	0.051	560	0.259 ± 0.021	0.716 ± 0.012
0.0505	0.102	560	0.613 ± 0.054	0.367 ± 0.057
0.0508	0.301	560	1.151 ± 0.03	-0.119 ± 0.02
0.0527	0.431	560	1.302 ± 0.034	-0.271 ± 0.0243
0.0208	0.08	406 ± 40	0.65 ± 0.02	0.35 ± 0.02
0.0202	0.123	433 ± 14	0.93 ± 0.01	0.087 ± 0.01
0.0205	0.163	350 ± 24	0.967 ± 0.02	-0.004 ± 0.01
0.0208	0.204	406 ± 31	1.15 ± 0.04	-0.12 ± 0.04
0.0204	0.245	785 ± 244	1.86 ± 0.39	-0.86 ± 0.41
0.0065	0.018	292 ± 61	0.14 ± 0.01	0.86 ± 0.01
0.00612	0.0373	350 ± 26	0.219 ± 0.019	0.804 ± 0.0102
0.00659	0.0514	381 ± 16	0.499 ± 0.008	0.5 ± 0.007
0.00655	0.0627	355 ± 20	0.68 ± 0.02	0.32 ± 0.02
0.0068	0.0754	377 ± 18	0.84 ± 0.02	0.18 ± 0.02
0.00681	0.112	334 ± 17	0.91 ± 0.02	0.11 ± 0.02
0.00692	0.188	361 ± 51	1.55 ± 0.14	-0.54 ± 0.15
0.0059	0.15	344 ± 35	1.39 ± 0.07	-0.37 ± 0.08
0.001	0.012	282 ± 24	0.158 ± 0.004	0.242 ± 0.05
0.001	0.03	261 ± 25	0.62 ± 0.02	0.38 ± 0.012
0.001	0.05	192 ± 21	0.86 ± 0.04	0.14 ± 0.002
0.001	0.101	190 ± 40	1.094 ± 0.001	-0.094 ± 0.0041

^a $[V] = 5.6 \times 10^{-4}$ M; temperature: 34.5°C .

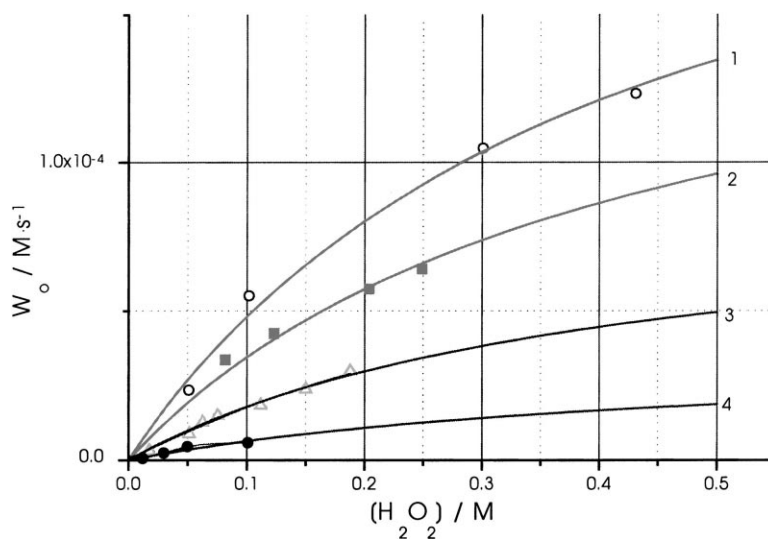


Fig. 4. The plot of the initial EA consumption rates (W_0) vs. initial hydrogen peroxide concentration ($[H_2O_2]_0$) at different initial concentrations of substrate. Conditions: $[V] = 5.6 \times 10^{-4}$ M, 34.5°C . (1) $[S]_0 = 0.05$ M; (2) $[S]_0 = 0.02$ M; (3) $[S]_0 = 0.006$ M; (4) $[S]_0 = 0.001$ M.

This fact is in line with the reaction scheme including only one active oxidant species, which reacts with all the substrates. The relative rates found for anthracenes are of the same order of magnitude, except for 9,10-dimethylanthracene, but are quite different from the literature data for the reactions of these substrates with free singlet dioxygen dissolved in acetone (see Table 2). The observed difference between two sets of data suggest that free singlet dioxygen is not involved in the reactions observed in the $V^V/H_2O_2/AcOH$ system.

In addition, the substrates like stilbene and other aryl- or alkyl-substituted alkenes, which are virtually inert toward free dissolved singlet dioxygen are readily oxidised with the $V^V/H_2O_2/AcOH$ system (see Table 2).

All the above data imply singlet dioxygen not to be the only (and at least not the main) oxidant species in the system. It seems that another intermediate is responsible for the substrate oxidation.

To elucidate the pathways of formation of the active oxidant and its reactivity we studied the kinetics of EA oxidation by hydrogen peroxide in the presence of vanadium(V) complexes in AcOH solution.

The EA consumption in the $H_2O_2/AcOH$ solution is at most 10% for 6 h in the absence of the catalyst. Therefore, non-catalyzed substrate oxidation can be neglected. The rate of EA oxidation increases directly with the catalyst concentration (Fig. 2).

The consumption of EA is described by exponential Eq. (9), approaching asymptotically a non-zero value (see Fig. 3, Table 3):

$$\frac{[S]}{[S]_0} = A_1 e^{-k_{\text{eff}} \tau} + y_0 \quad (9)$$

The value of the asymptotical limit depends on the initial concentrations of the oxidant and substrate

Table 4
The parameters of Eq. (11) at different initial EA concentrations^a

$[S]_0$ M	P_1 M s ⁻¹	P_2 M
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

^a $[V] = 5.6 \times 10^{-4}$ M; $[H_2O_2]_0 = 0.012\text{--}0.3$ M; temperature: 34.5°C .

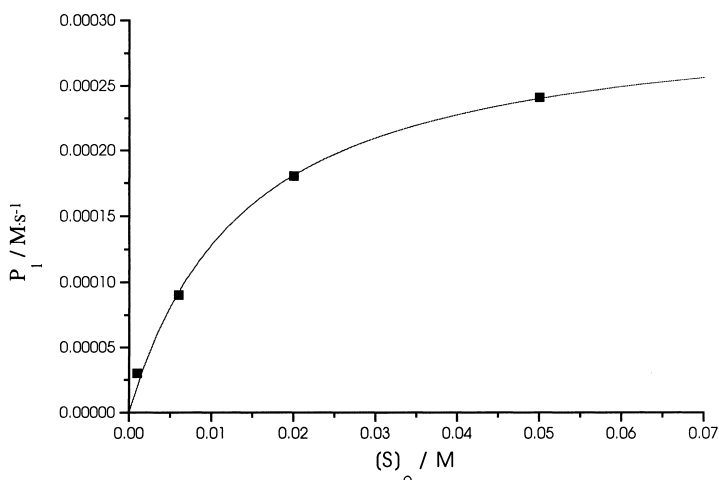


Fig. 5. Dependence of parameter P_1 on the EA initial concentration ($[S]_0$). Conditions: $[V] = 5.6 \times 10^{-4}$ M, 34.5°C .

(Fig. 3). The parameter y_0 in Eq. (9) becomes negative at a great excess of the oxidant ($[\text{H}_2\text{O}_2] > 0.2$ M). This fact indicates the zero (or close to zero) reaction order in the substrate concentration.

The additives of EAQ do not affect the rate of EA oxidation. Hence, the influence of the final reaction product on the reaction rate can be neglected.

In a series of experiments where the concentration of the substrate and other reaction conditions were

kept constant, the initial rates of EA oxidation calculated by Eq. (10)

$$W_0 = \left(-\frac{d[S]}{d\tau} \right)_0 = A_1 [S]_0 k_{ef} \quad (10)$$

increased with increasing initial H_2O_2 concentration (Fig. 4).

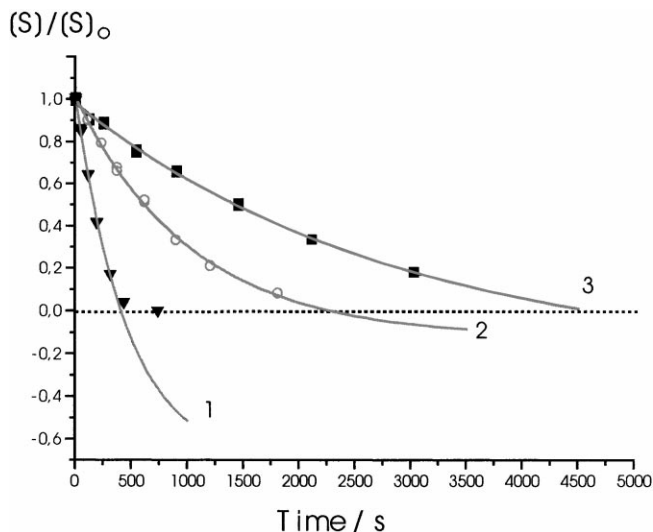


Fig. 6. The kinetic curves for EA conversion ($[S]/[S]_0$) at different water content. Conditions: $[S]_0 = 0.006$ M, $[\text{H}_2\text{O}_2]_0 = 0.144$ M, $[V] = 5.6 \times 10^{-4}$ M, 34.5°C . (1) No water added; (2) 2.6 M of water added; (3) 5 M of water added.

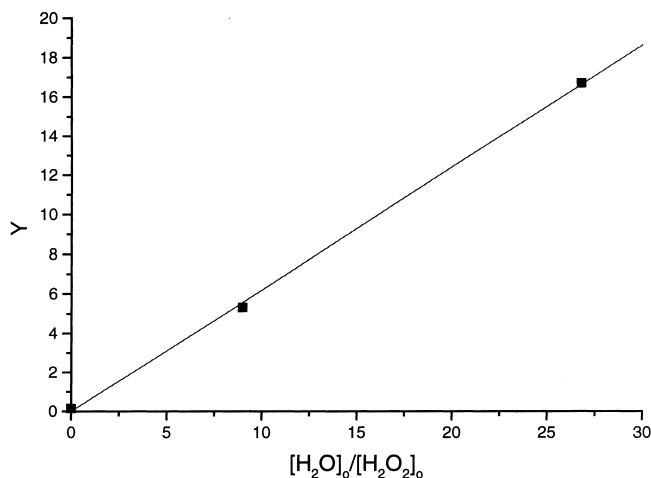


Fig. 7. The parameter $Y = \left\{ \frac{(P_4 + [S]_0)}{(W_0[S]_0 P_3)} - \left(\frac{P_2}{[H_2O_2]_0} - 1 \right) \right\}$ vs. $\left\{ \frac{[H_2O]_0}{[H_2O_2]_0} \right\}$ plot. Conditions: $[S]_0 = (5.66 \div 6.64)10^{-3}$ M, $[H_2O_2]_0 = 0.139 \div 0.144$ M, $[V] = 5.6 \times 10^{-4}$ M, 34.5°C .

The reaction rates obey the following equation:

$$W_0 = \frac{P_1[H_2O_2]_0}{P_2 + [H_2O_2]_0} \quad (11)$$

The values of parameters P_1 and P_2 are shown in Table 4 for the substrate concentrations of 0.001–0.0508 M in four experimental series. The parameter P_2 varies within the limits of its average value in all the four series, indicating that P_2 does not depend on the EA initial concentration.

The dependence of the parameter P_1 on the initial EA concentration (Fig. 5) can be approximated by the following relation:

$$P_1 = \frac{P_3[S]_0}{P_4 + [S]_0} \quad (12)$$

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

Hence, the kinetics of reaction (6) obeys the Michaelis–Menten equation:

$$W_0 = \frac{P_3[H_2O_2]_0[S]_0}{(P_2 + [H_2O_2]_0)(P_4 + [S]_0)} \quad (13)$$

The reaction rates increase with increasing $[H_2O_2]_0$ approaching a limit value, which depends on the first term in the denominator of Eq. (13). Within the Michaelis–Menten kinetic scheme, this fact suggests, for instance, that all the catalyst is bound to hydrogen peroxide forming a strong intermediate complex, which is low active in EA oxidation. The observed shape of the kinetic curves (see Figs. 3–5) can also be attributed to the formation of an inactive aqua complex of the catalyst due to the presence of water introduced together with H_2O_2 in the AcOH solution. For this reason we studied the effect of water additives on the reaction kinetics.

Our experiments showed that the water additives slow down the EA oxidation. However, the shape of the kinetic curves of substrate consumption in the presence of water does not change (Fig. 6), and, therefore, the form of Eq. (13) remains unchanged. The water effect cannot be rationalized as H_2O/EA competition for the coordination site at the vanadium(V) ion.² Therefore, the first term in the denom-

² The mechanisms of EA oxidation including intermediate complexes between EA and the catalyst should be ruled out because both the experimental data and conceptions of coordination chemistry on such a complexation with V^V are lacking.

inator of Eq. (13) also includes the retardation by H_2O :

$$W_0 = \frac{P_3 [H_2O_2]_0 [S]_0}{(P_2 + P_3 [H_2O]_0 + [H_2O_2]_0)(P_4 + [S]_0)} \quad (14)$$

or

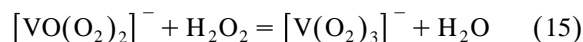
$$\frac{(P_4 + [S]_0)}{W_0 [S]_0 P_3} - \frac{P_2}{[H_2O_2]_0} - 1 = P_5 \frac{[H_2O]_0}{[H_2O_2]_0} \quad (14')$$

where $[H_2O]_0$ is the initial concentration of water, M.

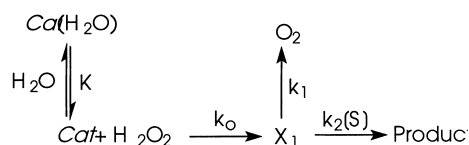
Eq. (14) well fits the experimental data with the average value $P_5 = 0.62 \pm 0.04$. As seen in Fig. 7, the experimental points lie on a straight line in the $\{((P_4 + [S]_0)/W_0 [S]_0 P_3) - ((P_2)/([H_2O_2]_0)) - 1\}$ versus $\{[H_2O]_0/([H_2O_2]_0)\}$ coordinates.

Two mechanistic schemes (see Schemes 2 and 3) can be used to rationalize the phenomena observed. Both schemes assume a steady-state approximation toward an active oxidant, which forms in the limiting stage.

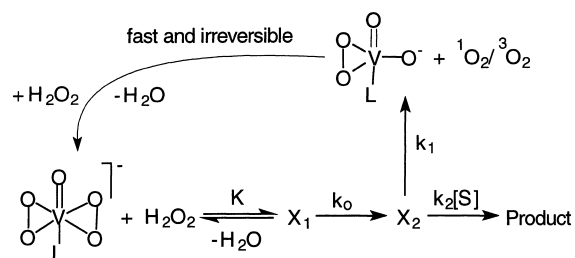
According to this scheme, the active intermediate X_1 , which is responsible for the EA oxidation and H_2O_2 decomposition, is formed via a reaction between H_2O_2 and the V^V complex. Based on the ^{51}V NMR data, diperoxo complex V^V of the $[V^V O(O_2)_2]^-$ type is the main form of V^V in the reaction solutions when $[H_2O_2]_0 = 0.1\text{--}1\text{ M}$. The NMR signal of the other V^V complexes were not found [13,14]. Hence, the symbol *Cat* in Scheme 2 is equal to $V^V O(O_2)_2^-$ and the stage of X_1 formation can be depicted by Eq. (15).



Hence, X_1 is assumed to be the $[V(O_2)_3]^-$ triperoxo



Scheme 2.



Scheme 3.

complex.³ Within the framework of this scheme, the retardation of reaction (6) by water could have been attributed to the reversible formation of a strong aqua complex which cannot for some reasons be converted into triperoxo complex.

However, our ^{51}V NMR data are in contradiction with this suggestion. Based on NMR data, diperoxo complexes are the main form of V^V compounds in the solution, and new signals do not appear after addition of water up to 2 M. This fact casts a doubt on the mechanistic Scheme 2.

According to this scheme, the triperoxo complex X_1 is formed from the most abundant complex $[VO(O_2)_2]^-$ by the replacement of the oxo ligand. Then, in the limiting stage, the complex X_1 transforms into the active intermediate X_2 , which either reacts with EA or decomposes evolving the O_2 molecule to form inactive vanadium compounds. In the framework of this scheme, the initial rate of reaction (6) can be written in the form:

$$W_0 = \frac{K [VO(O_2)_2] k_0 [H_2O_2]_0 [S]_0}{([H_2O]_0' + K [H_2O_2]_0)(k_1/k_2 + [S]_0)} \quad (16)$$

The initial total concentration $[H_2O]_0' = [H_2O]_0 + [H_2O]_0'' + \alpha [H_2O_2]_0$ includes the water added ($[H_2O]_0'$), the water content in the AcOH used ($[H_2O]_0'' = 0.8\text{ M}$), and the water introduced into the reaction solution with 17.8 M H_2O_2 aqueous solu-

³ The solvent (AcOH or H_2O) molecules are omitted for simplicity in the formulae of triperoxo and diperoxo complexes.

tion ($\alpha[\text{H}_2\text{O}_2]_0$, where $\alpha = 1.64$ is the ratio of the concentrations of water and hydrogen peroxide).

With allowance of these, Eq. (16) reduces to the form:

$$W_0 = \frac{(K[\text{cat}]k_0/(K + \alpha))[\text{H}_2\text{O}_2]_0[\text{S}]_0}{\left(\frac{[\text{H}_2\text{O}]''}{(K + \alpha)} + \frac{[\text{H}_2\text{O}]}{(K + \alpha)} + [\text{H}_2\text{O}_2]_0\right)\left(\frac{k_1}{k_2} + [\text{S}]_0\right)} \quad (17)$$

From a comparison of Eqs. (13) and (17) we obtain:

$$P_2 = \frac{[\text{H}_2\text{O}]_0''}{(K + \alpha)}; \quad P_3 = \frac{K[\text{cat}]k_0}{(K + \alpha)};$$

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

The value of $P_5 = P_2/[\text{H}_2\text{O}]_0''$ is equal to 0.5 ± 0.1 as far as the concentration of water in the solvent $[\text{H}_2\text{O}_2]_0'' = 0.8 \text{ M}$. The P_5 value found from independent kinetics data (see Eq. (14)) is equal to 0.62 ± 0.05 . So, both values coincide within the experimental error supporting the mechanistic Scheme 3. The equilibrium constant $K = (1/P_5) - \alpha = -0.03 \pm 0.1$ is small as compared to α , and the corresponding terms in the denominator of Eq. (17) can be neglected reducing it to Eq. (18).

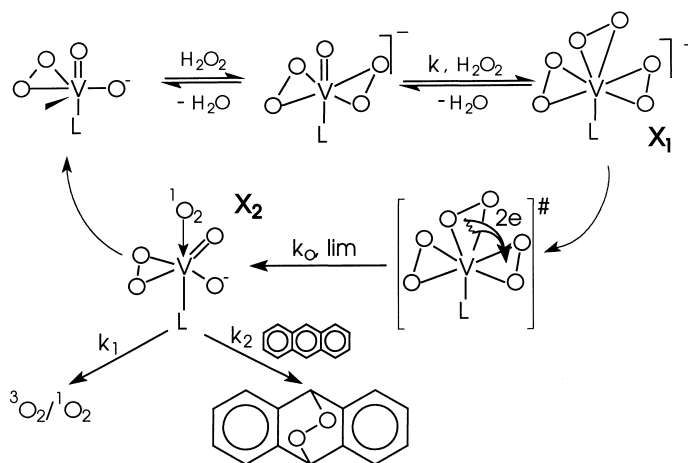
$$W_0 = \frac{K[\text{cat}]k_0[\text{H}_2\text{O}_2]_0[\text{S}]_0}{[\text{H}_2\text{O}]_0''\left(\frac{k_1}{k_2} + S_0\right)} \quad (18)$$

Based on Eq. (18), the observed shape of the kinetic curves (see Fig. 4) for reaction (6) with increasing $[\text{H}_2\text{O}_2]_0$ can be attributed to an increase in the

amount of water, which is introduced in the catalytic system together with aqueous hydrogen peroxide solution. Due to the competition between the H_2O_2 and H_2O molecules for the coordination site at the V^{V} ion, the concentration of the triperoxo complex is reduced as compared to that expected for the case when non-aqueous H_2O_2 is added. This is in a good agreement with our ^{51}V NMR data, which demonstrated predominance of the V^{V} diperoxo complexes in the course of experimental runs.

Thus, according to the data available the intermediate complex X_1 is formed from the diperoxo complex $[\text{VO}(\text{O}_2)_2]^-$ by the addition of the H_2O_2 molecule and detachment of H_2O molecule. In this reaction the O atom of the vanadyl group $\text{V}=\text{O}$ in the diperoxo complex is replaced for a peroxo group to form the triperoxo complex as shown in Scheme 4, where L is a solvent (H_2O or AcOH) molecule.

According to the Scheme 4, a vanadium(V)/singlet dioxygen complex X_2 is responsible for EA oxidation. The transformation of the intermediate complex X_1 into active oxidant X_2 is assumed to involve a two-electron transfer between two coordi-



Scheme 4. Mechanistic scheme for singlet dioxygen transfer to anthracene.

nated peroxy groups (in one step or in two one-electron successive steps). The inner-sphere formation of 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 give details of the composition and structure of the active oxidant species. Nevertheless, we can be assured with confidence that the active oxidant species is not the free singlet dioxygen and a vanadium(V) complex is donating singlet dioxygen to an anthracene molecule.

This statement is also supported by the following fact. Processing the changes in the initial reaction rates with a change in the initial EA concentration (Fig. 4) using Eq. (11), we can find the value of 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 deactivation of X_2 and k_2 is that of EA oxidation, respectively, see Table 5). From experiments on O_2 photooxidation of EA in AcOH solution [29,30], we have got the ratio of the 1O_2 quenching constant to that of the 1O_2 addition to EA molecule (see Table 5). A comparison of the ratios in Table 5 shows that the kinetic parameters related to X_2 differ remarkably from those of free 1O_2 . Moreover, X_2 is a much more effective oxidant toward EA than free 1O_2 dissolved in the same medium.

If the spin conservation rule is applicable to the $X_1 \rightarrow X_2$ interconversion, the molecule of dioxygen formed should be in a singlet state. In addition, the two occupied antibonding π^* -orbitals of the coordinated O_2^{2-} ligand in the complex X_1 are energetically non-equivalent. If the energy gap between these orbitals exceeds the energy of the triplet-singlet ($^3\Sigma_g \rightarrow ^1\Delta_g$) transition of the dioxygen molecule (23 Kcal mol $^{-1}$), then the formation of singlet dioxygen in the V^V coordination sphere of the complex X_2 is more favourable thermodynamically as compared to that of triplet dioxygen. Therefore, the pathway to the 1O_2 exciplex, X_2 , formation via

disproportionation of the O_2^{2-} ligands of the complex $V^V(O_2)_3^-$ (X_1) seems to be quite plausible.

4. Conclusive remarks

The nature of active species responsible for the transfer of singlet dioxygen from H_2O_2 to a substrate molecule in the $V^V/H_2O_2/AcOH$ oxidative system was elucidated from the kinetic data first obtained in this study. Our data imply that not less than 95% of EA is oxidized via the reaction with a vanadium(V) complex containing the 1O_2 molecule as a coordinated ligand. So, coordinated 1O_2 rather than free singlet dioxygen is the active oxidant in the system.

Alkene exciplexes, viz. complexes of the electron-excited species like singlet dioxygen with alkenes are well known from the Adam chemistry [33–35]. The data available on the photoinduced oxidation of alkenes, which contain H atom in the allyl position, point undoubtedly to the involvement of the intermediate π -complexes between the 1O_2 and the alkene molecules in the reaction. The intermediates of this type are responsible for the reaction stereochemistry [33].

The virtual $V^V(^1O_2)$ exciplex postulated in this work differs from those of the Adam chemistry as far as the vanadium(V) ion cannot be an electron donor. In this case, the 1O_2 molecule should have been stabilised through the donation of its electron pair to the vacant d-orbital of the vanadium ion. The interaction of the 1O_2 π -antibonding orbital with the electrons of the other ligands and the empty d-orbitals of V^V ion should be taken into account to discuss the stability and reactivity of the postulated $V^V(^1O_2)$ complex.

Inner-sphere two-electron transfer from one O_2^{2-} group to another peroxy group coordinated at the V^V ion leading to the active species X_2 (see Scheme 4) is an example of redox reactions catalyzed by metals with d^0 non-bonding configuration. The complex X_2 is assumed to contain the molecule of singlet dioxygen as a ligand. The effectiveness of complex X_2 in EA oxidation as compared to that of free 1O_2 dissolved in the reaction medium could be rationalized within two assumptions.

Table 5
Comparison of free and coordinated 1O_2 reactivities^a

Active oxidant	$k_q/k_s, M$
1O_2	0.15
X_2	0.014

^a $[H_2O]_{tot} = 3.64 M$; temperature: 34.5°C; k_q : oxidant deactivation rate constant; k_s : rate constant of oxidant with EA reaction.

1. The rate constant for the reaction of complex X_2 with EA is higher than that of free 1O_2 .
2. The life-time of complex X_2 is longer than that of 1O_2 in the same medium.

The formation of the V^V complex with 1O_2 due to a donor–acceptor interaction of the filled π^* -orbital of 1O_2 with vacant d orbitals of the central atom should enhance the electrophilicity of the coordinated 1O_2 . From another side, 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 participation of the V^V vacant d orbitals seems to be conceivable. Such an interaction could increase the occupation of the π^* -orbital of the coordinated 1O_2 and decrease its electrophilicity. Hence, both the life-time and reactivity of the coordinated 1O_2 molecule can be influenced by the ligand surrounding or solvent composition and the metal nature.

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