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Catalytic Peroxide Oxidation: The Structure of Key Intermediates in the V^V/H_2O_2 System According to Quantum Chemical Data

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Abstract—The inner-sphere isomerization of the peroxo complexes of vanadium(V) with the general formula $[VO_6]^-$ was studied using approximations based on the density functional theory (B3LYP/6-31G**) and the Møller-Plesset perturbation theory (MP2/6-31G**). It was found that the complex $[V(=O)(\eta O_2)(O_3)]^-$ containing the O_3 group as a bidentate ligand was the most stable isomer. The transition state region of a rearrangement of the triperoxo complex $[V(\eta O_2)_3]^-$ into $[V(=O)(\eta O_2)(O_3)]^-$ was localized. It was found that the activation barrier (~30 kcal/mol) was mainly due to O–O bond cleavage in the peroxo ligand. According to calculations, the reaction proceeds through two intermediate complexes whose structure can be interpreted as that containing coordinated singlet dioxygen (especially in the limiting case) because of noticeably shortened O–O bonds in the ηO_2 ligand. The calculated reaction scheme of the conversion of $[V(\eta O_2)_3]^-$ into $[V(=O)(\eta O_2)(O_3)]^-$ is qualitatively consistent with the previously found kinetics of the formation of ozone and the oxidation of alkanes, olefins, arenes, and singlet dioxygen traps.

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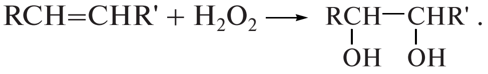
INTRODUCTION

The ability of vanadium(V) compounds to catalyze hydrocarbon oxidation is known since the classical study of Milas and Sussman [1], who found that V_2O_5 and a number of other transition metal oxides catalyze the hydroxylation of alkenes by hydrogen peroxide



$$\mathrm{RCH{=}CHR' + H_2O_2 \longrightarrow \underset{OH}{RCH}{-}\underset{OH}{CHR'}}\ .$$

More recently, it was found that almost all metal ions with the d^0 nonbonding configuration catalyze the epoxidation of alkenes by hydrogen peroxide or alkyl (aralkyl) hydroperoxides [2]. Epoxidation by *tert*-butyl hydroperoxide or β-phenylethyl hydroperoxide in the presence of titanium silicate or, under homogeneous conditions, molybdenum resinate has been industrially used [3]. A detailed study of the kinetics of propylene epoxidation by β-phenylethyl hydroperoxide in the presence of molybdenum resinate demonstrated for the first time the formation of a complex between the catalyst and the hydroperoxide [4–9].

It is believed that the peroxo complexes of metals play a role of key components in the catalyzed molecular reactions of H_2O_2 in solutions [10–13].

The number of coordinated peroxo groups varies depending on the ability of the metal atom to bind to the O_2 ligand, the concentration of hydrogen peroxide, and the pH of solution [14]. The study of the reactivity of the V^V/H_2O_2/RCOOH system revealed the following unusual facts:

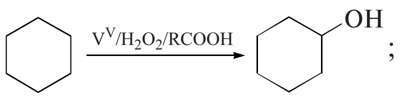
the release of singlet dioxygen in the decomposition of H_2O_2 [15]

$$2H_2O_2 \longrightarrow {}^1O_2 + 2H_2O;$$

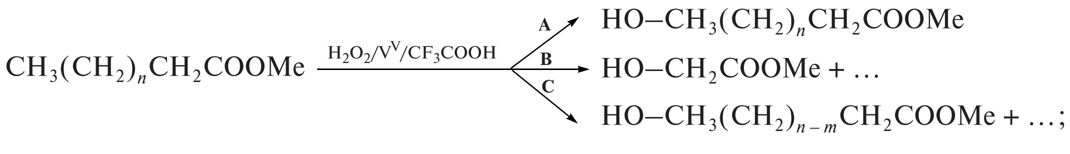
the formation of ozone [16]

$$3H_2O_2 \longrightarrow O_3 + 3H_2O;$$

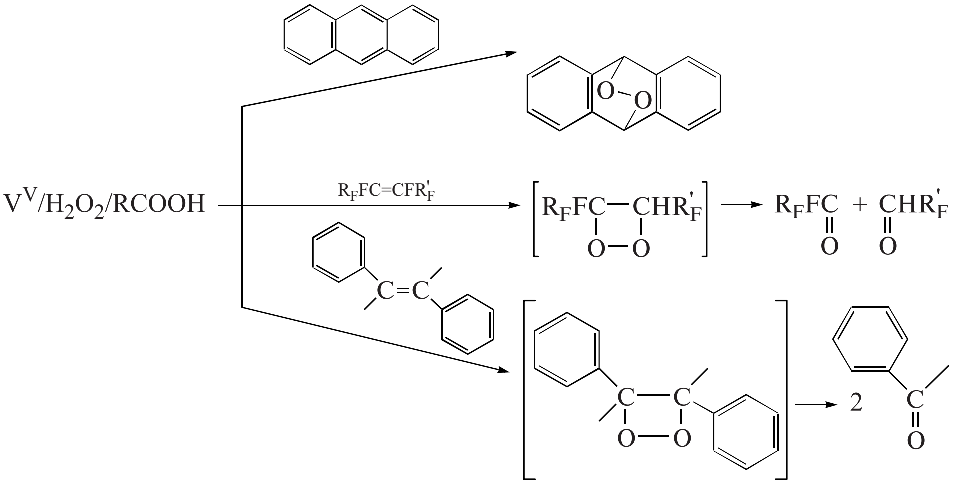
the ability of peroxo complexes to transfer singlet dioxygen to acceptors such as anthracene [17], perfluoroalkenes [18], and stilbene [19] (Scheme 1) the ability of peroxo complexes to hydroxylate alkenes with C–H bond cleavage [20]



the oxidation of fatty acid esters with not only C–H (reaction path **A**) but also C–C bond cleavage (reaction paths **B** and **C**) [21]



$$CH_3(CH_2)_nCH_2COOMe \xrightarrow{H_2O_2/V^V/CF_3COOH} \begin{cases} \xrightarrow{A} HO{-}CH_3(CH_2)_nCH_2COOMe \\ \xrightarrow{B} HO{-}CH_2COOMe + \ldots \\ \xrightarrow{C} HO{-}CH_3(CH_2)_{n-m}CH_2COOMe + \ldots; \end{cases}$$



Scheme 1.

the oxidation of molecular nitrogen [22]

$$N_2 + H_2O_2 \xrightarrow{H_2O_2,\ AcOH,\ V^V} N_2O + H_2O.$$

The ^{51}V NMR spectra indicated the occurrence of monoperoxo $[V(=O)_2(\eta O_2)]^-$ and diperoxo $[V(=O)(\eta O_2)_2]^-$ complexes in the $V^V/H_2O_2/RCOOH$ system [23]. The study of the kinetics of oxidation of anthracenes [17, 23] suggests the intermediate formation of triperoxo $[V(\eta O_2)_3]^-$ complexes.[1] It is evident that data on the structures of the above peroxo compounds are of paramount importance for the interpretation of the observed catalytic reactions [15–21].

Unfortunately, the low stability of peroxo complexes in solutions does not allow one to unambiguously determine their structures experimentally. Detailed information on the structures of peroxo complexes in a solid phase can be obtained using X-ray diffraction analysis [24]; however, as is customary, problems related to the low symmetry of compounds of this kind make high-quality single crystals difficult to prepare. It is even more difficult to obtain experimental data on the mechanism of mutual transformations in these complexes.

Because of this, the quantum chemical simulation of the structure of metal peroxides is of considerable current interest. This approach seems a real way to obtain data that are necessary for the interpretation of experimental results concerning both the physicochemical properties and reactivity of this class of compounds.

This work was devoted to a quantum chemical study of the structures and inner-sphere transformations of the oxygen-containing complexes of vanadium(V).

CALCULATION PROCEDURE

At the first stage, we found the equilibrium geometric configurations of peroxo complexes with a full parameter optimization in the Gaussian 03 package [25] using the DFT method with the B3LYP hybrid exchange-correlation potential [26, 27] and the 6-31G** AO basis set. The calculated harmonic vibration frequencies demonstrated that the detected structures correspond to true minimums in potential energy curves. The found geometric configurations of the complexes were also used as starting points for optimization in an approximation based on the second-order Møller-Plesset perturbation theory (MP2) with the same 6-31G** basis set. The harmonic vibration frequencies were also calculated using the MP2 method. To refine the relative energy values, corrections for zero-vibration energy were also made.

In particular, the QST2(3) method was used to search for transition states [28, 29]. Harmonic vibration frequencies were calculated for all of the saddle points found.

RESULTS AND DISCUSSION

Metavanadate Anion

Crystalline salts with the metavanadate anion VO_3^- were not detected, and it is likely that the salts of this anion do not exist in aqueous solutions. However, there are many hydrated forms of this anion [30]. Our calculations predicted that the isolated metavanadate anion $[V(=O)_3]^-$ has the shape of an equilateral triangle D_{3h} with V=O multiple bonds of equal length (1.642 or 1.715 Å for B3LYP or MP2, respectively);

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[1] None of the formulas takes into consideration the possible binding of the V atom to solvent molecules.

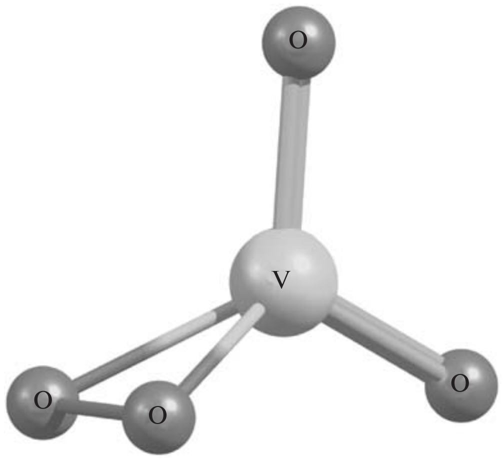

Fig. 1. Monoperoxovanadate **I**.

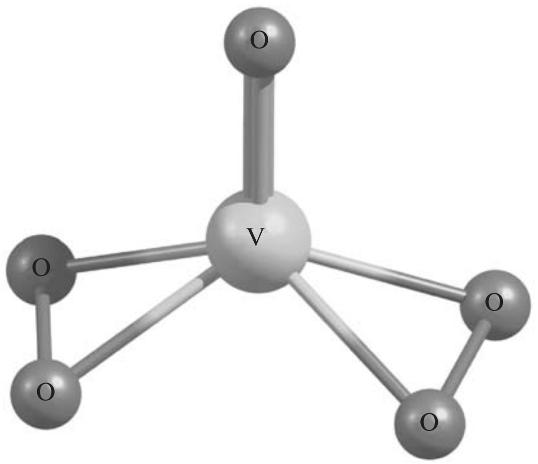

Fig. 2. Diperoxovanadate **II**.

this is consistent with the conclusions made by Vyboishchikov and Sauer [31].

Monoperoxovanadate

The crystals of a vanadium(V) complex containing a peroxo ligand and two vanadyl groups were not isolated, and its structure was not studied experimentally. The monoperoxo complexes of vanadium(V) with chelating ligands are known, and they have been studied [32]. Our calculation performed for the simplest complex containing no compound ligands demonstrated that four oxygen atoms in the isolated monoperoxovanadate ion $[V(=O)_2(\eta O_2)]^-$ (**I**, Fig. 1) are arranged at the corners of a quasi-tetrahedron: the O=V=O group and the η-peroxo metallocycle lie in perpendicular planes. In this case, the VO_4 “tetrahedron” is strongly distorted because the V=O bonds are shorter than the V–O bonds in the η-peroxo metallocycle and the O–O bond length and distances between the oxygen atoms of the peroxo group and the oxygen atoms of vanadyl groups are strongly different (Table 1). The O=V=O, O–V–O, and O=V–OO bond angles are also considerably different from the tetrahedral angle (Table 1). The vanadium atom is shifted to the axial oxygen atom and arranged above the plane of the oxygen atoms of the peroxo ligand and one of the vanadyl groups because of the strong trans effect of the axial O atom [33]; this is typical of metal complexes with the d^0 configuration containing an M=O group [34]. The data obtained are also consistent with the results of calculations performed using the B3LYP method with the TZVP basis set [31] (Table 1).

Diperoxovanadate

In the isolated diperoxovanadate ion $[V(=O)(\eta O_2)_2]^-$ (**II**, Fig. 2), the coordination center is a distorted tetragonal pyramid, where the oxygen atoms of two ηO_2 groups lie in the same plane to form an isosceles trapezoid (Fig. 2). Both of the ηO_2 groups are equivalent. However, we found that the V–O interatomic distances in the $V(O_2)$ groups are noticeably different (Table 2) unlike the case of **I**. The vanadium atom is shifted to the oxygen atom of the vanadyl group for the same reasons as in **I**.

A comparison of the results of calculations with data obtained by X-ray diffraction analysis (Table 2) suggests that the calculations were performed correctly.

Triperoxovanadate

Elemental analysis [37] and mass-spectrometric data [38] are available for vanadium(V) complexes containing three peroxo groups $[V(\eta O_2)_3]^-$. However, there are no published X-ray diffraction data on the structure of these complexes.

Complex **IIIa** (Fig. 3) contains two equivalent ηO_2 ligands, whose four oxygen atoms form an isosceles trapezoid as in diperoxovanadate **II**. The V–O bond lengths and O–V–O bond angles of asymmetric $V(\eta O_2)$ metallocycles in **II** and **IIIa** are also similar (Table 1). The third ηO_2 ligand occupies an axial position (its plane is almost perpendicular to the trapezoid base). Differences in the V–O interatomic distances[2] of this ligand are much more pronounced than in the groups that form the equatorial plane: one V–O bond in this asymmetric metallocycle is the shortest (1.754 Å), whereas the second is the longest among all of the V–O bonds of the complex (1.915 Å) (Table 1). In other words, complex **IIIa** is geometrically similar to diperoxovanadate **II**, in which an additional oxygen atom is attached to the vanadyl group. It is likely that, in the presence of a substrate with clearly pronounced acceptor properties, this oxygen atom can leave the peroxo ligand and complex **IIIa** can be converted into diperoxovanadate **II**.

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[2] Hereinafter, B3LYP/6-31G** calculation data are used, unless otherwise specified.

Table 1. Main geometry characteristics of the coordination polyhedrons of peroxo complexes according to B3LYP/6-31G** calculation data

Parameter	$[V(=O)_2(\eta O_2)]^-$ **I**	$[V(\eta O_2)_2(\eta)\overset{V}{O}_2]^-$ **IIIa**	$[V(\eta O_2)_3]^-$ **IIIb**	$[V(=O)(\eta O_2)(O_3)]^-$ **IV**	$V[(=O)_2(\eta O_2)O_2]^-$ **V**	$V[(=O)_2(\eta O_2)_2]^-$ **VI**
∠O=V=O	113.8	–	–	–	112.8	–
∠O=V–O	119.9	–	–	110.0	–	115.5, 106.3
∠O–V–O	48.0	47.0	47.8	47.3	41.8	40.3
V=O	1.620 [1.630]	–	–	1.589	1.609, 1.615	1.600, 1.672
V–O (in ηO_2)	1.833 [1.850]	1.794, 1.850	1.819	1.827	1.918, 1.951	1.947, 1.985
O–O (in ηO_2)	1.491 [1.490]	1.455	1.475	1.466	1.380	1.354
V–O (in asymm. $\eta\overset{V}{O}_2$)	–	1.754, 1.915	–	–	–	–
O–O (in asymm. $\eta\overset{V}{O}_2$)	–	1.470	–	–	–	–
V–O (in coord. $^1O_2$)	–	–	–	–	2.010	–
O–O (in coord. $^1O_2$)	–	–	–	–	1.275	–
V–O (in coord. O_3)	–	–	–	1.914, 1.984	–	–

Note: B3LYP/TZVP calculation data [31] are given in square brackets. Interatomic distances and bond angles are expressed in angstrom units and degrees, respectively.

Note that the B3LYP/6-31G** calculations led us to a conclusion that structure **IIIb** of the anion $[V(\eta O_2)_3]^-$ can exist (Fig. 4); the stability of this anion is somewhat lower than that of complex **IIIa** (~3 kcal/mol). This isomer of triperoxovanadate **IIIa** has a propeller-shaped structure in which all of the oxygen atoms are equivalent and the V–O interatomic distances and O–V–O bond angles in peroxo ligands are almost the same as those in monoperoxovanadate **I** (Table 1). This result should be considered with caution because it was not supported by MP2 calculations.

Ozone is released upon the decomposition of hydrogen peroxide in trifluoroacetic acid in the presence of V^V compounds. This reaction can be explained in terms of a scheme that involves oxygen atom transfer to the neighboring peroxo group with the formation of a precursor of molecular ozone, for example, a complex with the O_3 ligand,[3] the subsequent degradation of which can lead to the release of ozone [39]. It is likely that the inner-sphere oxidation of the O_3 group by the peroxo ligand coordinated to the same V^V atom is favorable because the oxidant occurs in the same complex and the approach of reactants and additional structure rearrangements are not required. The appearance of two thermodynamically stable vanadyl groups from a peroxo ligand in the course of inner-sphere oxidation can compensate the consumption of

Table 2. Main geometry parameters of diperoxovanadate **II** according to B3LYP/6-31G** calculation data

Bond length, Å		Bond angle, deg	
V–O (oxo)	1.597 **(1.603)**	O=V–O	111.1, 116.8
V–O $(\eta O_2)_{cis}$	1.808 **(1.866)**	O–V–O (ηO_2)	47.21 **(45.93)**
V–O $(\eta O_2)_{trans}$	1.859 **(1.903)**	V–O_{cis}–O_{trans}	68.2 **(68.4)**
O–O (ηO_2)	1.469 **(1.471)**	V–O_{trans}–O_{cis}	64.6 **(65.7)**

Note: X-ray diffraction data [35, 36] are given in parentheses.

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[3] The coordinated O_3 bidentate ligand is usually referred to as the ozonide dianion O_3^{2-}.

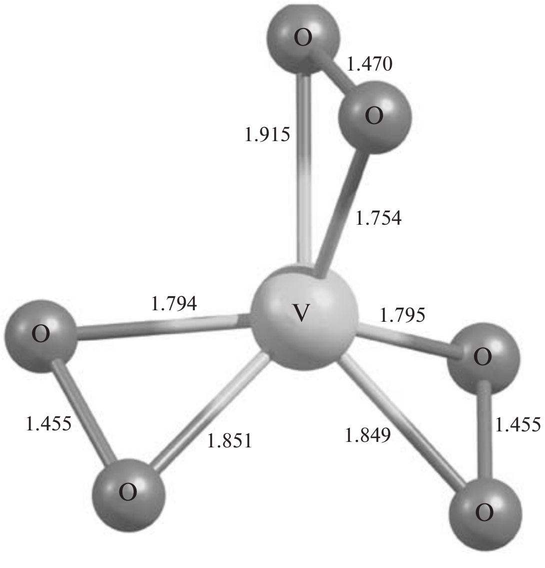
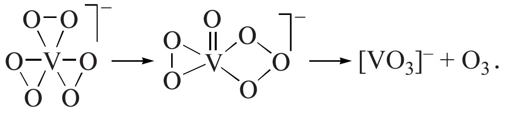


Fig. 3. Triperoxovanadate **IIIa**.

energy for the removal of electrons from the coordinated O_3 ligand:



III **IV** (I)

Complex with the Coordinated O_3 Ligand (IV, Fig. 5)

The ozonides of phosphorus [40] and alkali metals [41] are well known; however, transition metal complexes containing ligands of this kind were not described. At the same time, quantum chemical simulation data [42] suggest that these complexes can occur.

According to our calculations (for a gas phase), the energy of the complex $[V(=O)(\eta O_2)(O_3)]^-$ is lower than that of the triperoxo complex by ~15 kcal/mol (Fig. 6). The oxygen atom of the vanadyl group occupies an axial position in complex **IV**, whereas the peroxo group and the oxygen atoms of the ozonide group coordinated to the vanadium atom form an equatorial plane. The central oxygen atom of the O_3 group is arranged above the equatorial plane in close proximity to the vanadium atom (Table 1). Similarly to an allyl ligand, the O_3 group forms the base of a distorted pyramid with the vanadium atom at the vertex [43].

The V–O bond lengths in the ηO_2 ligands are the same (1.827 Å) and almost equal to the average value for these bonds (~1.83 Å) in various peroxo complexes of vanadium $[VO_n]^-$ ($n = 4, 5$) (Table 3). On the contrary, two V–O bonds in the O_3 ligand are noticeably elongated (1.914 Å), and the interatomic distance with the central oxygen atom of this ligand is even greater (1.984 Å) so that it is likely that the third V–O bond is not formed here, the more so because the charge on this oxygen atom is extremely small (<0.2 e). At the same time, the NBO analysis suggests the absence of this bond, whereas atoms-in-molecules (AIM) analysis indicates the occurrence of a critical point, which corresponds to a weak bond. It is more likely that this inconsistence suggests the localization of a considerable electron density within the V–O_3 metallocycle (according to data obtained by both of the methods, the total negative charge on the O_3 ligand is close to unity), which increases its stability as a whole, rather than the formation of an additional V–O bond. The lengths of O–O bonds in both of the ligands (~1.47 Å) are typical of the well-known peroxo complexes of vanadium. Thus, complex **IV** can be considered as that containing the ozonide ligand in an anionic form.

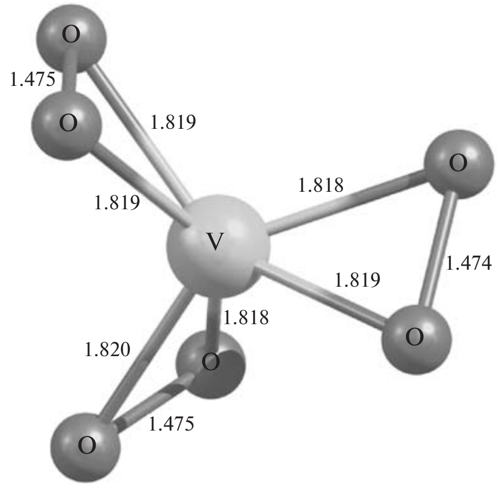


Fig. 4. Triperoxovanadate **IIIb**.

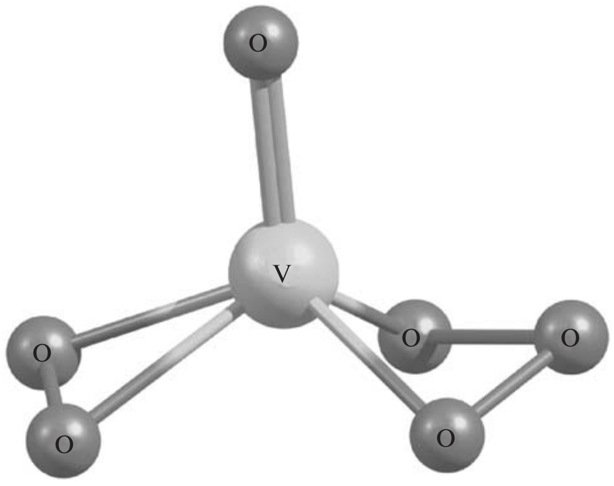


Fig. 5. Vanadium(V) complex with a coordinated ozonide dianion **IV**.

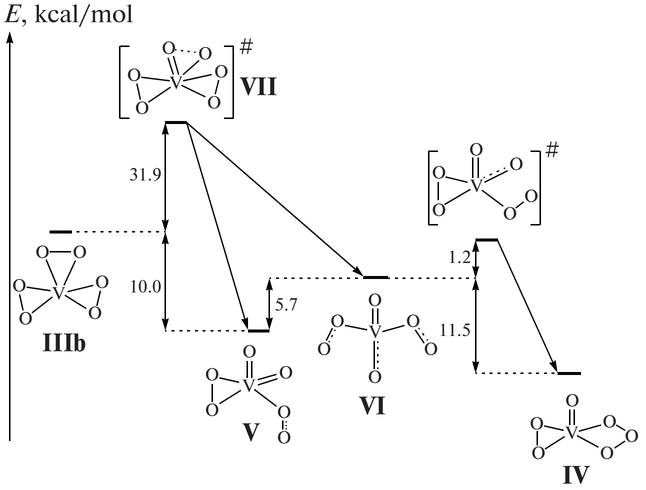


Fig. 6. Inner-sphere transformations of peroxo complexes.

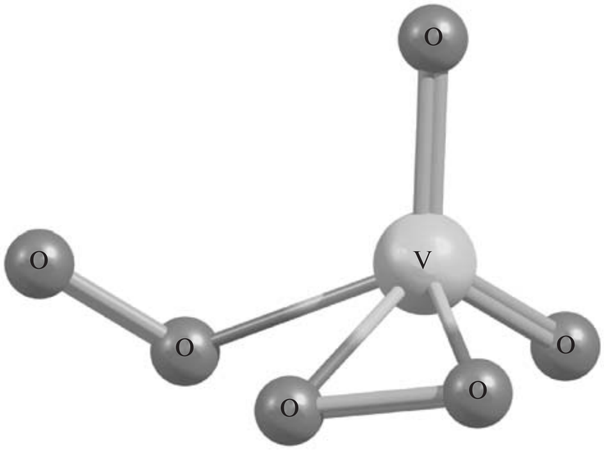


Fig. 7. Complex **V**.

The formation of ozone from the O_3 group in reaction (I) requires the two-electron oxidation of this ligand as a result of the action of an outer- or inner-sphere agent.

Possible Active Intermediates of Hydroperoxide Oxidation in the V^V/H_2O_2 System

It was demonstrated experimentally that intermediates formed from a complex of V^V with three peroxo ligands are responsible for the oxidation of alkanes, anthracene, and its derivatives in the V^V/H_2O_2 system [20, 21]. The structures of these intermediates are unknown.

In the localization of the transition state region of reaction (I), we found that the rearrangement of complex **IIIa** into complex **IV** occurs through the intermediate formation of at least two components (**V** and **VI**, Figs. 7 and 8, respectively), which correspond to local minimums in the potential energy surface (Fig. 6). Energy differences between complexes **V** and **VI** are small, and the exothermic transitions **III** $\longrightarrow$ **V** and **III** $\longrightarrow$ **VI** occur with close activation barriers (~30 kcal/mol). This value is much lower than the O–O bond cleavage energy; that is, we can assume that the role of the central atom consists in the stabilization of a migrating oxygen atom by its coordination.

Table 3. Electron and geometry characteristics of $[V(=O)_{3-k}(\eta O_2)_k]^-$ complexes ($k = 0$–3)

Properties	Method	Complex	$[V(=O)_3]^-$	$[V(=O)_2(\eta O_2)]^-$ **I**	$[V(=O)(\eta O_2)_2]^-$ **II**	$[V(\eta O_2)_3]^-$ **IIIa**
V	Charge Q[V]	B3LYP	1.596	1.586	1.543	1.553
		MP2	2.143	2.148	2.115	2.119
(=O)	Charge Q[O]	B3LYP	−0.865	−0.776	−0.668	–
		MP2	−1.048	−0.954	−0.835	–
	$R_{V=O}$, Å	B3LYP	1.642	1.620	1.597	–
		MP2	1.715	1.685	1.649	–
(ηO_2)	Charge Q[O–O]	B3LYP		−1.034	−0.937	−0.851
		MP2		−1.238	−1.140	–
	R_{V-O}, Å	B3LYP		1.832	1.834	1.826
		MP2		1.883	1.871	–
	R_{O-O}, Å	B3LYP		1.491	1.469	1.455
		MP2		1.534	1.510	–

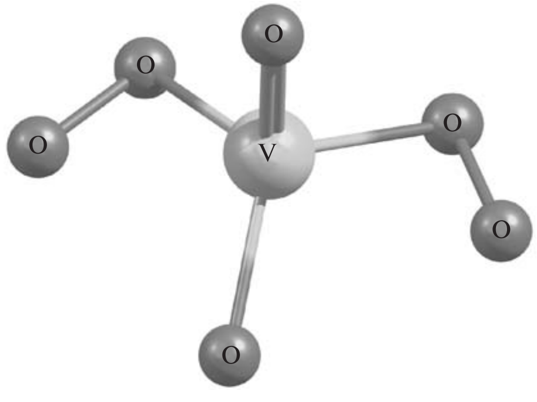


Fig. 8. Complex **VI**.

Note that the transition states found by both of the methods for the transitions **III** ⟶ **V** and **III** ⟶ **VI** are very similar in terms of structure and energy (structure **VII**, Fig. 9), although this is likely due to the limited capabilities of these methods.

According to calculated data,[4] the geometry of complexes **V** and **VI** is much different from the geometries of triperoxo complex **IV** and transition state **VII**. The coordination of one of the dioxygen fragments in structure **V** (Fig. 7) is analogous to the angular coordination of molecular oxygen in hemoglobin and salene complexes [44]. The O–O distance (1.275 Å) is only 0.06 Å longer than the bond length in the free $^1O_2$ molecule [45], whereas the shortest V–O distance is ~2 Å, which is typical of the donor–acceptor V–O bond [24]. The distance between the other O atom and the vanadium atom in this fragment is 2.794 Å, which is greater than the sum of the covalent atomic radii of V and O (~2 Å), to suggest the absence of bonding between these atoms. The second dioxygen fragment is similar to the peroxo ligand with a shortened O–O distance (1.380 Å), which is noticeably smaller than the O–O distance in the well-known peroxo complexes (1.45–1.46 Å) [24].

Complex **VI**, whose geometry is generally similar to that of diperoxovanadate **II**, contains two quasi-peroxo groups, in which neither O–O nor V–O distance is characteristic of peroxo ligands (Fig. 8). The V–O distances in the ligands under consideration (1.947 and 1.985 Å) are much longer than bonds in the η-peroxo group of complex **II** (~1.83 Å). The NBO analysis of the structure of complex **VI** indicates that the O–O fragment is bound to the vanadium(V) atom by only a single V–O bond. The O–O distance in complex **VI** (1.355 Å) is much shorter than that in complex **II** (1.469 Å).

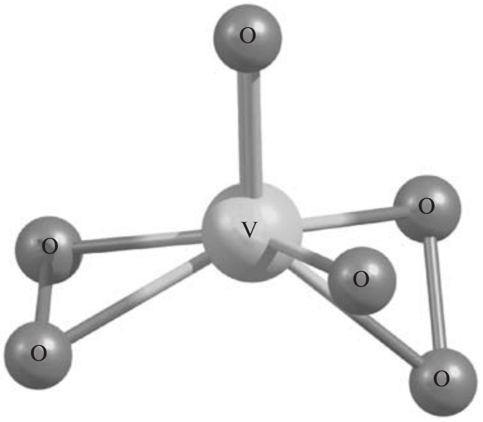


Fig. 9. Transition state **VII** in the conversion of triperoxovanadate **III** into intermediate complexes **V** and **VI** in the complexation reaction of vanadium(V) with the coordinated ozonide dianion.

Thus, in spite of some structural differences, complexes **V** and **VI** are similar in the occurrence of two O_2 fragments with considerably shortened O–O bonds and elongated V–O bonds in either of them. That is, we can hypothesize that these complexes can be the carriers of $^1O_2$ to a substrate under certain conditions.

In kinetic experiments, it was found that a complex carrier of singlet dioxygen to a substrate is formed at a rate-limiting step of anthracene oxidation in the $V^V/H_2O_2/AcOH$ system from the triperoxo complex of vanadium(V) [46]. In this case, anthracene is converted into endoperoxide in ~90% yield. The amount of singlet oxygen released into the volume is 10% regardless of the presence or absence of anthracene (Fig. 10).[5] These facts suggest that the complex carrier of singlet dioxygen and the complex responsible for the release of free singlet dioxygen are different compounds (Scheme 2).

Scheme 2 is consistent with both experimental and calculated data. For example, a high energy barrier for the conversion of the triperoxo complex into active oxidation intermediates **V** and **VI** suggests that this step can be slow, as follows from a kinetic experiment [46]. The release of singlet dioxygen from the triperoxo complex, which requires a considerable inner-sphere rearrangement, also occurs slowly. At the same time, intermediates **V** and **VI** contain fragments similar to coordinated singlet dioxygen; it is likely that they play the role of singlet dioxygen carriers to the substrate molecule. In terms of Scheme 2 (path **A**), this transfer occurs rapidly and does not limit substrate

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[4] Both the MP2 and B3LYP methods led to the same conclusions on the structures of complexes **V** and **VI**. The geometry parameters of these compounds are similar in terms of both of the approximations.

[5] We are grateful to Professor A.A. Krasnovskii, Cand. Sci. (Biol.) Yu.V. Kovalev (Moscow State University), Dr. Sci. (Chem.) D.V. Kazakov, and Cand. Sci. (Chem.) D.V. Mal'tsev (Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences) for their assistance in the determination of the yield of released $^1O_2$.

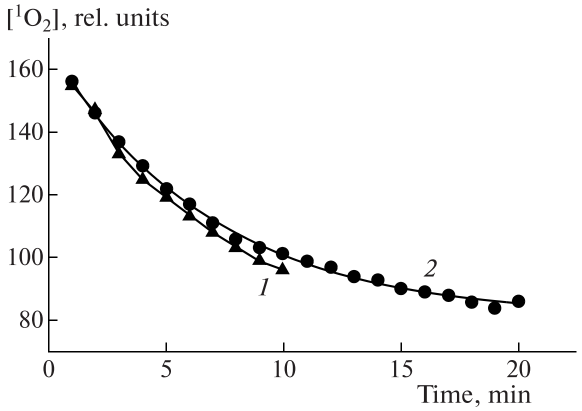


Fig. 10. Phosphorescence intensity of $^1O_2$ formed in the V^V/H_2O_2/AcOH system (*1*) in the absence and (*2*) in the presence of 2-ethylanthracene. $[H_2O_2] = 1$ mol/l; $[V^V] = 10^{-2}$ mol/l; [Substr] = 0.02 mol/l; 15°C.

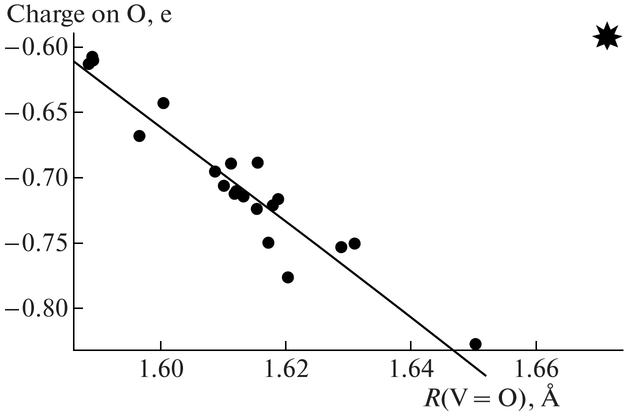
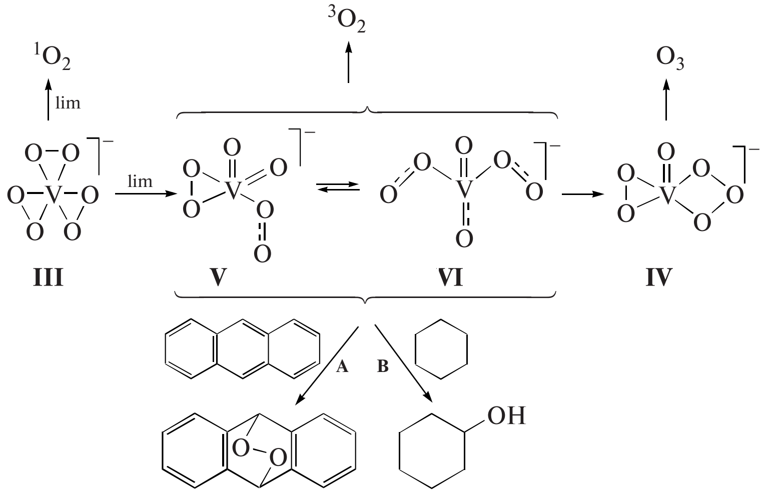


Fig. 11. Correlation between the V–O bond length of the vanadyl group and the charge on the oxygen atom of this group. ✸ marks the charge on the O atom of the long V–O bond of complex **VI**.

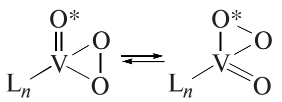


Scheme 2. Mutual transformations of vanadium complexes and the reaction paths of $^1O_2$, $^3O_2$, and O_3 formation: Anthracene and cyclohexane oxidation

oxidation for an appropriate acceptor of $^1O_2$, such as substituted anthracene.

Another special feature of complex **VI** is that, of two V–O oxo groups, only one axial group (1.600 Å) is a typical vanadyl group, whereas the other (equatorial, 1.672 Å) is nonequivalent to the first not only geometrically. Using the B3LYP method for vanadyl groups in a great number of calculated peroxo and hydroperoxo complexes, we found that a linear correlation occurs between the V–O distance in the vanadyl group and the charge on the oxygen atom of this group; in this case, the charge on the oxygen atom decreases (becomes more negative) with increasing the V–O interatomic distance (Fig. 11). The charge of the O atom in the short axial V=O group of complex **VI** lies in the correlation curve, whereas the charge on the O atom of the long V–O group in the equatorial plane is arranged much higher than the correlation straight line; that is, it is absolutely inconsistent with the common trend for this type of complexes. This lability (structural flexibility) explains the small activation barrier of the transition of **VI** to **IV**, which occurs with the participation of the oxygen atom of the long V–O group.

The fact that the exchange of oxygen atoms between the peroxo ligand and the vanadyl group was detected in the decomposition of $H_2{}^{18}O_2$ in water in the presence of vanadium(V) compounds [47] indirectly suggests the structural flexibility of the test complexes:



In the course of oxidation in the $V^V/H_2O_2/AcOH$ catalytic system, singlet dioxygen or a singlet oxygen atom is transferred to the anthracene molecule or cyclohexane, respectively. In simultaneous oxidation, cyclohexane and 2-ethylanthracene are consumed in parallel reactions [48]; that is, both of the substrates either react with the same active intermediate or different active intermediates are responsible for singlet dioxygen and singlet oxygen atom transfer and the transition between these active intermediates occurs with a low activation energy and, consequently, rapidly.

Intermediates **V** and **VI**, whose structures were revealed by quantum chemical calculations, are consistent with both of the proposed mechanisms. Thus, indeed, according to calculations, these complexes are readily converted into each other (Fig. 6), and we can hypothesize that both of the intermediates can transfer singlet dioxygen to a substrate.

CONCLUSIONS

The quantum chemical simulation of the structure and inner-sphere reactions of vanadium(V) peroxo complexes revealed a number of important special features, which could not be a priory hypothesized and found by other methods. The conclusion on the structural flexibility of the nearest environment in oxygen-excessive vanadium complexes with the d^0 configuration and the general formula $[VO_6]^-$ can be considered as the main result. The previously proposed hypothesis on the existence of complexes with the coordinated O_3 ligand was supported. The geometry of the $V(O_3)$ fragment resembles the π-allyl ligand, which is well known in the chemistry of organometallic compounds.

It was demonstrated that the formation of a complex with an ozonide ligand occurs through two intermediate complexes (**V** and **VI**), which correspond to local minimums in the potential energy surface. According to calculated data, complexes **V** and **VI** can serve as a carrier of singlet dioxygen $^1O_2$ to a substrate. All of these results are reasonably consistent with experimental data obtained in the oxidation of anthracene and its derivatives in the $V^V/H_2O_2/RCOOH$ system.

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