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Oxidative transformations in the $V^V/H_2O_2/RCOOH$ system†

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In order to reveal the nature of intermediates of peroxide oxidation catalysed by vanadium compounds, the inner-sphere transformations of vanadium(V) peroxo complexes with the general formula $[VO_6]^-$ has been studied in approximations of the density functional theory (B3LYP/6-31G**) and Møller–Plesset perturbation theory (MP2/6-31G**). It has been found that the triperoxo complex $[V(\eta\text{-}O_2)_3]^-$ undergoes isomerization to a complex that is unexpectedly more stable, $[V(=O)(\eta\text{-}O_2)(O_3)]^-$, which incorporates an O_3 group as a bidentate ligand. This reaction was found to occur *via* two intermediate complexes that can transfer both singlet dioxygen and an oxygen atom to a substrate molecule. The reaction scheme proposed on the basis of calculations is in qualitative agreement with the previously obtained kinetic regularities of ozone formation and oxidation of alkanes, alkenes, arenes and singlet dioxygen acceptors in the $V^V/H_2O_2/RCOOH$ catalytic system.

Hydroperoxide oxidation is a traditional method in synthetic organic chemistry.[1] Fenton, Haber and Weiss, Baeyer and Villiger, Prilezhaev, Pisarzhevskii, Shpital'skii, Udris and Hock who made the most significant contribution to the chemistry of hydrogen peroxide and its derivatives are among the most prominent researchers in the history of science. Reactions catalysed by molybdenum[2] and titanium[3,4] compounds have found industrial application. The kinetics and mechanism of propylene epoxidation with α-phenylethylhydroperoxide in the presence of molybdenum complexes have been studied by Gavrilenko *et al.*[5–7]

It is generally accepted that peroxo complexes of transition metals are catalysts or active intermediates in hydroperoxide oxidation reactions.[8] The composition of the coordination sphere and the type of coordination of the peroxo ligand depend on the nature of the central atom and on the composition of the reaction medium, and they are a matter of discussion in most cases.

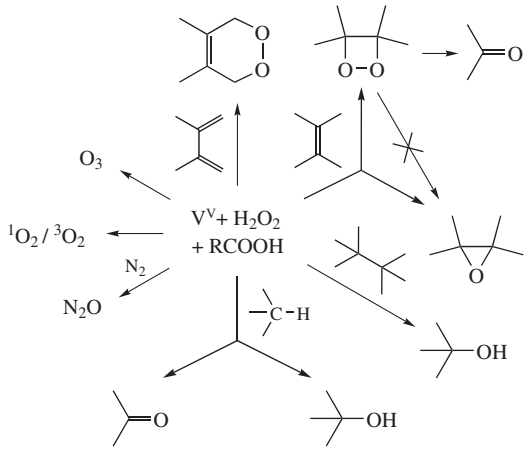
The capability of vanadium(V) compounds to catalyse the oxidation of hydrocarbons has been known since the classical study by Milas and Sussman,[9] who have found that V_2O_5 and oxides of some other transition metals catalyse the hydroxylation of alkenes with hydrogen peroxide.

$$RHC{=}CHR' + H_2O_2 \longrightarrow \underset{OH\ \ OH}{RHC{-}CHR'}$$

In this work, we summarise the results of studies on the $V^V/H_2O_2/RCOOH$ system. Our experiments have shown that this system can cleave C–C and C–H bonds in alkanes,[10] the C=C bond in alkenes,[11] transfer a singlet dioxygen molecule to substrates capable of diene synthesis[12] and oxidise molecular nitrogen.[13] Furthermore, $O_2(^1\Delta_g)$[14] and ozone[15] are generated in the system (Scheme 1).

Left to right: **Alexander A. Markov**, junior scientist of Laboratory of Metal-complex Catalysis of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences (IGIC RAS), graduated from Voronezh State University (2005); **Sergei P. Dolin**, graduated from M. V. Lomonosov Moscow State University (1966), Ph.D. in chemistry (1973), head of Laboratory of Quantum Chemistry of the IGIC RAS; **Natalia I. Moiseeva**, graduated from M. V. Lomonosov Moscow Institute of Fine Chemical Technology (MIFCT) (1974), Ph.D. in chemistry (1993), Senior scientist at the Laboratory of Metal-complex Catalysis of the IGIC RAS; Academician **Ilya I. Moiseev**, graduated from MIFCT (1952), full member of the RAS (1992), full member of Academia Europaea (London, 1994), full member of Academia Scientiarum et Artium Europaea (Vienna, 1996), Vice-President of D. I. Mendeleev Russian Chemical Society (2000), full member of the Academy of Sciences, Arts and Literature (Paris, 2002), winner of A. P. Karpinsky Prize (1999), Triumph Prize (2002), RF State Prize (2003); awarded the Silver medal and delivered a series of lectures (Centenary Lecture) at the Royal Society of Chemistry, UK (2007), the supervisor of RAS research directions 'Metal Complex Catalysis' and 'Coordination Chemistry', Chief researcher at the Laboratory of Metal-complex Catalysis of the IGIC RAS, Professor at I. M. Gubkin Russian State University of Oil and Gas; Professor **Alexander E. Gekhman**, graduated from MIFCT (1972), Corresponding member of the RAS (2000), head of Laboratory of Metal-complex Catalysis of the IGIC RAS. In the picture one can see a portrait of Academician **Yakov K. Syrkin** (1894–1974), an authors' predecessor and teacher.

† Dedicated to Professor Roger A. Sheldon in the recognition of his outstanding contribution in oxidation catalysis.



Scheme 1 Reactivity of the V^V/H_2O_2/RCOOH catalytic system.

For example, 2-ethylanthracene, a typical acceptor of singlet dioxygen, is smoothly oxidised in the V^V/H_2O_2/AcOH system to give 2-ethylanthraquinone. The ethyl group is not involved in the reaction, which suggests that this system contains no free radicals.

9-Methylanthracene, 9,10-dimethylanthracene and 9,10-diphenylanthracene are oxidised in a similar way.

Experiments on cyclohexane oxidation have shown that the complex(es) formed in this system not only insert one oxygen atom into a substrate C–H bond but also convert the substrate to a ketone. Nevertheless, these diverse reactions occur in parallel: when cyclohexane and cyclohexanol are concurrently oxidised in the test system, neither the accumulation rates of both products nor the final concentration of cyclohexanone depend on the starting concentration of cyclohexanol. Thus, the alcohol is neither an intermediate nor a ketone precursor.

Oxidation of linear alkanes in acetic acid involves only C_{sec}–H bonds and is not accompanied by oxidative destruction of the substrate. Conversely, oxidation of branched hydrocarbons results in destruction of the carbon skeleton at a rate comparable to those of 'normal' hydroxylation and ketonation.

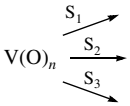
In the same system, methyl esters of fatty acids not only undergo hydroxylation like cyclohexane but also, like alkanes with iso-structures, enter a reaction that is new for linear hydrocarbons and involves cleavage of the C-C bond. For example, the oxidation of methyl octanoate gives products with the same hydrocarbon chain length as the original ester, along with three isomers of hydroxyheptanoic acid, three isomers of hydroxyhexanoic acid, three isomers of hydroxypentanoic acid, two isomers of hydroxybutanoic acid and even glycolic acid.

In trifluoroacetic acid, such stable compounds as α- and β-perfluoroalkenes, perfluoroarenes, nitrobenzene *etc.* undergo oxidation with cleavage of the C=C bond,[15] and even such an inert substrate as molecular nitrogen undergoes oxidation to give a small amount of nitrous oxide detected by chromatography–mass spectrometry.[13]

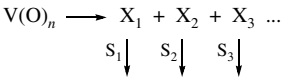
We did not observe any indication of the involvement of free radicals in any of the cases studied.

Thus, all of the above facts suggest that the V^V/H_2O_2/RCOOH catalytic system features multiple types of reactivity. There are three possible explanations to this phenomenon, *viz.*

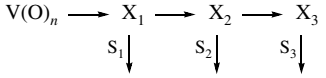
(i) coordination compounds containing one or more peroxo ligand(s) can react with different oxidisable substrates:



(ii) a few compounds of this kind are simultaneously present in the system:



(iii) reactive intermediates are formed in succession:



Kinetic analysis[15] has led to the conclusion that the latter variant really occurs.

The ^{51}V NMR spectra show that monoperoxo $[V(=O)_2(\eta\text{-}O_2)]^-$ and diperoxo $[V(=O)(\eta\text{-}O_2)_2]^-$ complexes exist in the V^V/H_2O_2/RCOOH system.[16]

Even the first kinetic studies[16,17] have shown that the vanadium(V) complex responsible for the reactions involves at least three peroxo groups, that is, six oxygen atoms. Therefore, at the first stage of studies on the details of the mechanism of oxidative reactions, it seemed worthwhile to consider the structure and intra-sphere reactions of the $[VO_6]^-$ complex in the gas phase.

Computational procedure

At the first stage, we found the equilibrium geometrical configurations of peroxo complexes with full parameter optimization in the Gaussian 03 program[18] using the DFT method using hybrid exchange correlation potential B3LYP[19,20] and the AO 6-31G** basis. Calculations of the frequencies of harmonic vibrations confirmed that the discovered structures match the true minima on the potential curves. Furthermore, the resulting geometrical configurations of the complexes were used as the starting point for optimization in the approximation of the second-order Møller–Plesset perturbation theory (MP2) with the same basis, 6-31G**. The MP2 method was also used to compute the harmonic vibration frequencies. To refine the relative energy values, corrections for the energy of zero vibrations were introduced.

According to ^{51}V NMR spectral data, peroxovanadates, including $[V(O_2)_3]^-$, are diamagnetic;[21] therefore, only the spin-restricted versions of the above methods were used.

The methods used to search for transition states included QST2(3).[22,23] Frequencies of harmonic vibrations were computed for all the saddle points found.

Structure and properties of the peroxo group in vanadium(V) complexes‡

Monoperoxovanadate. Crystals of the vanadium(V) complex containing a peroxo ligand and two vanadyl groups have not been isolated, and its structure has not been studied experimentally. Monoperoxo complexes of vanadium(V) with chelating ligands are known.[24] A computation§ that we made for a simplest complex containing no complex ligands showed that four oxygen atoms in an isolated monoperoxovanadate anion $[V(=O)_2(\eta\text{-}O_2)]^-$ **1** (Figure 1) are arranged in the corners of a strongly distorted quasi-tetrahedron: the O=V=O moiety and the η-peroxo metal ring lie in perpendicular planes; the V=O bonds are shorter than

‡ The formulas of peroxo complexes are given without consideration of possible binding of the V atom with solvent molecules.

§ Unless indicated otherwise, the data provided in the text below correspond to B3LYP/6-31G** calculations.

Table 1 The main geometrical parameters of coordination polyhedra of peroxo complexes according to B3LYP/6-31G** calculations. The values in square brackets show data of B3LYP/TZVP calculations.[27] Interatomic distances are provided in Å and bond angles are shown in degrees.

Parameters	$[V(=O)_2(\eta\text{-}O_2)]^-$ **1**	$[V(\eta\text{-}O_2)_3]^-$ **3a**	$[V(\eta\text{-}O_2)_2(\eta\text{-}O_2')]^-$ **3b**	$[V(=O)(\eta\text{-}O_2)(O_3)]^-$ **4**	$V[(=O)_2(\eta\text{-}O_2)O_2]^-$ **5**	$V[(=O)_2(\eta\text{-}O_2)_2]^-$ **6**
∠O=V=O	113.8	—	—	—	112.8	—
∠O=V–O	119.9	—	—	110.0	—	115.5, 106.3
∠O–V–O	48.0	47.8	47.0	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 $\eta\text{-}O_2$)	1.833 [1.850]	1.819	1.794, 1.850	1.827	1.918, 1.951	1.947, 1.985
O–O (in $\eta\text{-}O_2$)	1.491 [1.490]	1.475	1.455	1.466	1.380	1.354
V–O (in asymmetric $\eta\text{-}O_2'$)	—	—	1.754, 1.915	—	—	—
O–O (in asymmetric $\eta\text{-}O_2'$)	—	—	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	—	—

the V–O bonds in the η-peroxo metal ring, while the O–O bond length differs strongly from the distance between the O atoms of the peroxo group and the O atoms of the vanadyl groups (Table 1). The O=V=O, O–V–O and O=V–OO bond angles also differ considerably from the tetrahedral angle (Table 1). The vanadium atom is displaced towards the axial oxygen atom and is located above the plane where the oxygen atoms of the peroxo ligand and one of the vanadyl group lie, which results from a strong trans-effect of the axial O atom[25] and is typical of metal complexes with d^0 configuration containing an M=O group.[26] The data obtained are in good agreement with the results of B3LYP calculations with TZVP basis[27] (Table 1).

Diperoxovanadate. The coordination node of the isolated diperoxovanadate anion $[V(=O)(\eta\text{-}O_2)_2]^-$ **2** (Figure 1) is a distorted tetragonal pyramid, where the oxygen atoms of the two equivalent peroxo groups are located in the same plane, thus forming an equilateral trapezium. However, unlike in compound **1**, the V–O interatomic distances in each $V(\eta\text{-}O_2)$ moiety differ markedly (Table 2). For the same reasons as in **1**, the vanadium atom is displaced towards the oxygen atom of the vanadyl group.

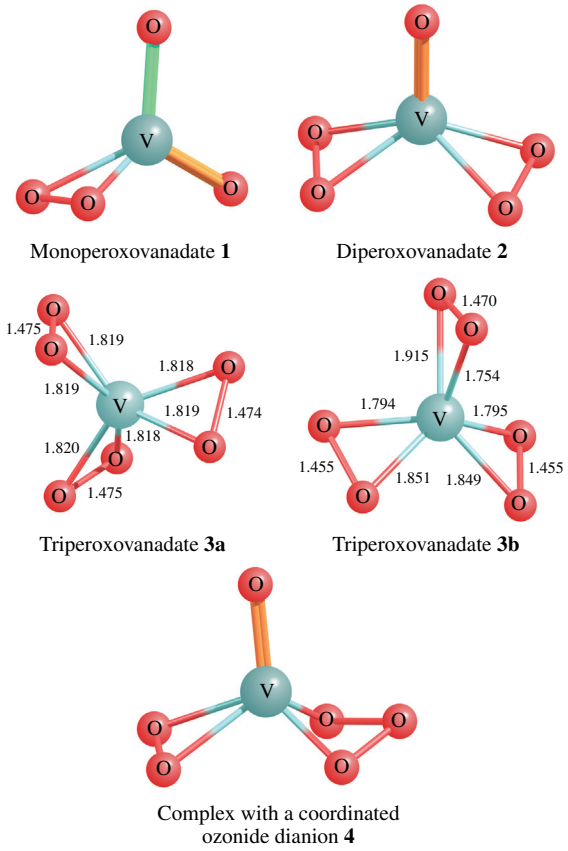


Figure 1 Molecular structures of complexes **1**, **2**, **3a**, **3b** and **4**. Bond lengths for **3a** and **3b** are given in Å.

The quantum-chemical simulation results are in good correlation with experimental X-ray diffraction data (Table 2).

Triperoxovanadate. There are no reliable published data, including X-ray diffraction, on the structure of vanadium(V) complexes with three peroxo groups of the type $[V(\eta\text{-}O_2)_3]^-$. B3LYP/6-31G** calculations have shown that two conformations of the $[V(\eta\text{-}O_2)_3]^-$ anion can exist, namely, symmetric **3a** and asymmetric **3b** (Figure 1), the structure and properties of which will be considered below. Triperoxovanadate isomer **3a** has a propeller-like structure, in which all oxygen atoms are equivalent, while the V–O interatomic distances and O–V–O bond angles in the peroxo ligands are similar to those in monoperoxovanadate **1** (Table 1).

According to B3LYP/6-31G** calculations, the formation energy of triperoxovanadate **3b** and a water molecule from diperoxovanadate **2** and hydrogen peroxide is approximately 9.2 kcal mol^{-1}. Hence, it can be expected that such complexes will be formed in solutions containing hydrogen peroxide.

It is significant that the O–O interatomic distances in all complexes listed above are nearly the same as those experimentally found for H_2O_2: 1.47 Å (gas) and 1.46 Å (solid).[28]

Other calculations[29] have also led to the conclusion on the existence of highly symmetrical triperoxo complex **3a**. However, our MP2 calculations resulted in the conclusion that there is no minimum on the potential surface that corresponds to complex **3a**. So, even if such a complex is formed according to B3LYP data, it is converted to **3b**, a compound that is less symmetric but more stable.

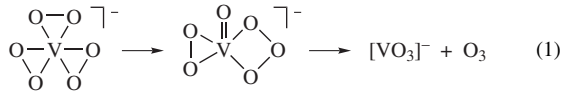
Structure and reactions of complex 3b‡

Complex **3b** (Figure 1) contains two equivalent η-coordinated O_2 ligands, whose four oxygen atoms form an equilateral trapezium like in diperoxovanadate **2**. The V–O bond lengths and O–V–O bond angles in asymmetric metal cycles $V(\eta\text{-}O_2)$ in **2** and in **3b** are also similar (Table 1). The third O_2 ligand occupies an axial position (its plane is almost perpendicular to the trapezium base). The differences between the V–O interatomic distances‡ of this ligand are much more pronounced than in the groups that form the equatorial plane: one V–O bond in the asymmetric metallocycle is the shortest (1.754 Å), whereas the other one is the longest among all V–O bonds of complex **3b** (1.915 Å) (Table 1). In other words, the geometry of complex **3b** resembles diperoxovanadate **2**, in which an

Table 2 The main geometrical parameters of diperoxovanadate **2** according to B3LYP/6-31G** calculations. The values in parentheses show X-ray diffraction data.[40,41]

Bond	Bond length/Å	Angle	Angle value/°
V–O (oxo)	1.597 (1.603)	O=V–O	111.1, 116.8
$V\text{–}O\ (\eta\text{-}O_2)_{cis}$	1.808 (1.866)	O–V–O ($\eta\text{-}O_2$)	47.21 (45.93)
$V\text{–}O\ (\eta\text{-}O_2)_{trans}$	1.859 (1.903)	$V\text{–}O_{cis}\text{–}O_{trans}$	68.2 (68.4)
O–O ($\eta\text{-}O_2$)	1.469 (1.471)	$V\text{–}O_{trans}\text{–}O_{cis}$	64.6 (65.7)

additional oxygen atom is 'attached' to the vanadyl group. This oxygen atom may leave the peroxo ligand in the presence of a substrate with pronounced acceptor properties, and complex **3b** can be converted into diperoxovanadate **2**. Decomposition of hydrogen peroxide in trifluoroacetic acid in the presence of V^V compounds produces ozone. This reaction can be explained within the scheme involving the transfer of an oxygen atom to an adjacent peroxo group to give a complex with an O_3^- ligand;¶ subsequent decomposition of the latter may result in the release of ozone.[30,††]



3 **4**

The complex with coordinated O_3 ligand 4

Phosphorus ozonides[31] and alkali metal ozonides[32] are well known; however, no transition metal complexes containing such ligands have been reported.

According to our calculations,§ the energy of the $[V(=O)(\eta\text{-}O_2)(O_3)]^-$ complex is lower by ~15 kcal mol^{-1} than that of the triperoxo complex (Figure 2). The oxygen atom of the vanadyl group occupies the axial position in complex **4**, whereas the peroxo group and the oxygen atoms of the ozonide group coordinated with the vanadium atom form the equatorial plane. The central oxygen atom of the O_3 group is located above the equatorial plane at rather a small distance from the vanadium atom (Table 1). Like the allyl ligand, the O_3 group occupies the base of a distorted pyramid with a vanadium atom in a vertex.[33] However, in the case of allyl-type coordination, all three oxygen atoms must be bound to the vanadium atom. NBO analysis has shown that the population of the contact of the central atom of the O_3 group with the vanadium atom is negligibly small; that is, this group is bound to the metal atom like the trimethylene ligand. On the other hand, analysis by AIM (Bader's 'atoms in molecules') method shows the existence of a critical point corresponding to a weak bond. This discrepancy most likely gives evidence in favour of localization of a considerable electron density inside the $V(O_3)$ metallocycle (according to

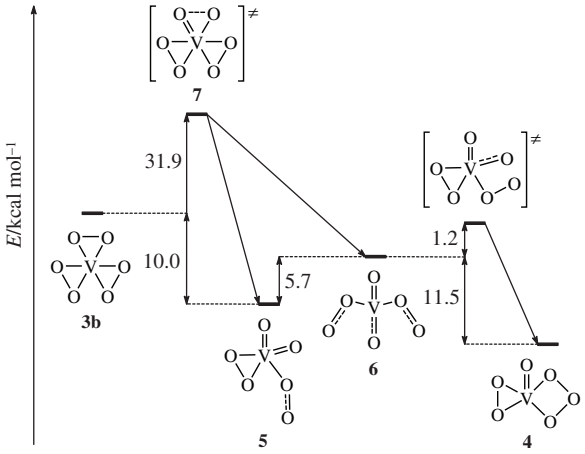
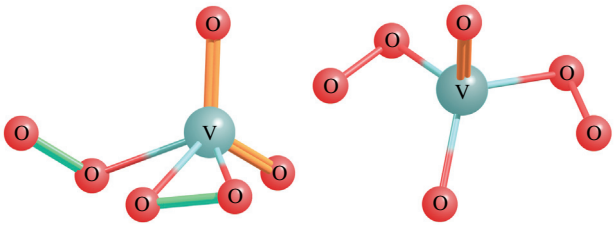


Figure 2 Inner-sphere transformations of peroxo complexes.

¶ The bidentate-coordinated O_3 ligand is usually referred to as 'the O_3^{2-} ozonide dianion' in the literature.

†† The evolution of ozone due to inner-sphere oxidation of the O_3 group by the peroxo ligand is probably facilitated due to the fact that the oxidant is located in the same complex and no approximation of reagents or additional structural rearrangements are required. The formation of two thermodynamically stable vanadyl groups from the peroxo ligand during inner-sphere oxidation can compensate the energy consumption for the removal of electrons from the coordinated O_3 ligand.



5 **6**

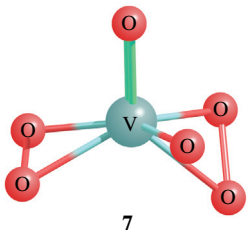
Figure 3 Molecular structures of complexes **5** and **6**.

data of both methods, the total negative charge on the O_3 ligand is close to unity), which increases its stability as a whole, rather than in favour of the formation of an additional V–O bond. The lengths of O–O bonds in O_3 and O_2 ligands (~1.47 Å) are typical of known vanadium peroxo complexes.

Localization of the region of the ozone formation transition state in reaction (1) showed that rearrangement of complex **3b** to complex **4** occurs through the intermediate formation of at least two complexes **5** and **6** (Figure 3) corresponding to local minima on the potential energy surface (Figure 2). The energy difference between complexes **5** and **6** is small and exothermic transitions **3** → **5** and **3** → **6** occur with similar activation barriers (~30 kcal mol^{-1}). This value is much smaller than the O–O bond breakdown energy; *i.e.*, it may be assumed that the role of the central atom involves stabilisation of the migrating oxygen atom by its coordination. Note that the transition states for the transitions **3** → **5** and **3** → **6** found by both methods are similar in both structure (**7**, Figure 4) and energy. It may not be excluded, however, that the conclusion about the identity of the transition states for the two reactions in question results from limited capabilities of the calculation methods.

According to calculation data,‡‡ the geometry of complexes **5** and **6** differs considerably from those of triperoxo complex **3** and transition state **7**. The coordination of one dioxygen fragment in structure **5** is similar to the angular coordination of molecular oxygen in haemoglobin and in salen complexes.[34] The O–O distance (1.275 Å) is just 0.06 Å larger than the bond length in a free $^1O_2$ molecule,[35] whereas the shortest V–O distance is ~2 Å, which is typical of the V–O donor-acceptor bond.[36] The distance between the other O atom and the vanadium atom in this fragment is 2.794 Å, which exceeds the total of the covalent radii of the V and O atoms (~2 Å); this is evidence of the absence of bonding between these atoms. The second dioxygen fragment resembles a peroxo ligand with a shortened O–O distance (1.380 Å), which is noticeably shorter than the O–O distance in the known peroxo complexes (1.45–1.46 Å).[36]

Complex **6** (Figure 3), whose overall geometry resembles diperoxovanadate **2**, contains two quasi-peroxo groups where neither O–O not V–O distances are typical of peroxo ligands. The V–O distances in the ligands in question are considerably



7

Figure 4 Transition state **7** for the conversion of **3** to intermediate complexes **5** and **6** in the formation of the vanadium(V) complex with a coordinated ozonide dianion.

‡‡ Both MP2 and B3LYP methods provide the same conclusions on the structures of complexes **5** and **6**. The values of geometrical parameters for these compounds are similar for both approximations.

longer (1.947 and 1.985 Å) than the bonds in the peroxo group of complex **2** (~1.83 Å). NBO analysis of the structure of complex **6** shows that the O–O fragment, whose length is much smaller (1.355 Å) than that in diperoxo complex **2** (1.469 Å), is bound with the vanadium(V) atom by only one V–O bond.

Thus, despite certain differences in structure, the common feature of complexes **5** and **6** is that each of them contains two O_2 fragments with considerably shortened O–O bonds and elongated V–O bonds. Hence, it may be assumed that these complexes can act as carriers of $^1O_2$ to the substrate under certain conditions.§§

Possible reactive intermediates of hydroperoxide oxidation in the V^V/H_2O_2 system

Studies on the reactivity of the V^V/H_2O_2/RCOOH system revealed the following unusual reactions.

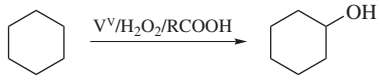
1. Ozone formation[15]

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

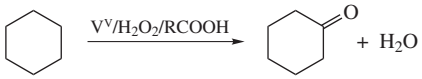
2. Evolution of singlet dioxygen upon H_2O_2 decomposition[14]

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

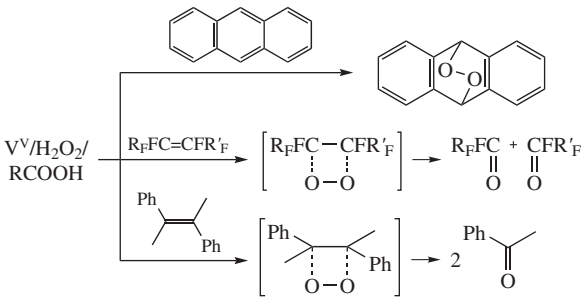
3. Ability of peroxo complexes to hydroxylate alkanes with cleavage of a C–H bond.[10,37]



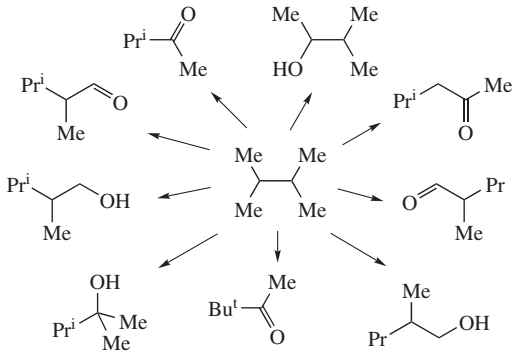
4. Oxidation of cyclohexane into cyclohexanone.[37]



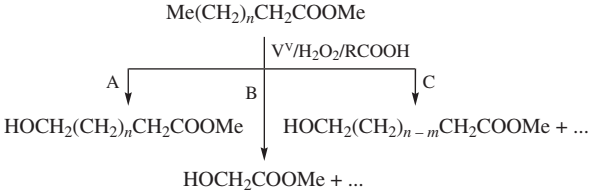
5. Ability of peroxo complexes to transfer singlet dioxygen to such acceptors as anthracene,[12] perfluoroalkenes[15] and stilbene.[11]



6. Skeleton breakdown in branched alkanes accompanied by shortening of the carbon chain and migration of alkyl groups, including methyl group.[10]



7. Oxidation of fatty acid esters with cleavage of not only C–H (route A) but also C–C bonds (routes B and C).[10]



8. Oxidation of molecular nitrogen[13]

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

The combination of results obtained in studies on the reaction kinetics and by quantum-chemical simulation allows us to make assumptions on the nature of complexes responsible for above reactions.

In fact, kinetic experiments have shown that, in anthracene oxidation in the V^V/H_2O_2/AcOH system, a complex that carries singlet dioxygen to the substrate is formed from vanadium(V) triperoxo complex at the limiting step.[12] As a result, anthracene is converted to the *endo*-peroxide in ~90% yield. The amount of singlet dioxygen evolved into the medium is ~10% irrespective of the presence or absence of anthracene (Figure 5),¶¶ whereas the amount of molecular oxygen evolved into the medium decreases abruptly (Figure 6). These facts imply that the complex that carries singlet dioxygen to the substrate and the complex responsible for the evolution of free singlet dioxygen are different compounds (see Scheme 2, reactions of complexes **3**, **5** and **6**, route A).

Scheme 2 is consistent with both experimental and computational data. For example, the high energy barrier in conversion of

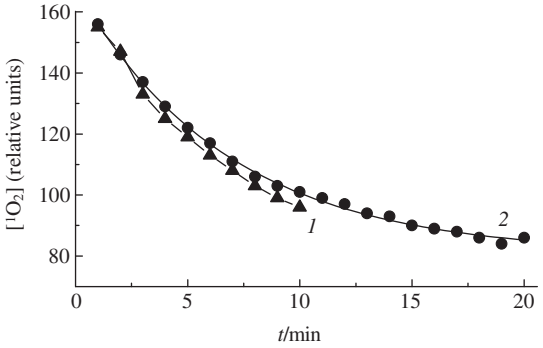


Figure 5 Phosphorescence intensity of $^1O_2$ formed in the V^V/H_2O_2/AcOH system (*1*) in the absence and (*2*) in the presence of 2-ethylanthracene. $[H_2O_2]$ = 1 mol dm^{-3}, $[V^V]$ = 0.01 mol dm^{-3}, [Substr] = 0.02 mol dm^{-3}, 15 °C.

§§ All peroxovanadates are diamagnetic.[21] Meanwhile, the calculated O–O distances (1.38 Å) are characteristic of superoxide systems, which might be evidence of the biradical structure of complexes **5** and **6**. Calculations on the triplet state of these complexes by spin-unrestricted B3LYP and MP2 methods give contradictory results: MP2 calculations do not result in an equilibrium configuration, whereas UB3LYP/6-31G** gave only one steady-state point corresponding to the equilibrium geometry of complex **6**. The energy of this complex in the triplet state is unexpectedly lower by 34 kcal mol^{-1} than that in the singlet state. However, these results should be treated with caution, since the use of single-determinant methods is not quite correct for the description of open-shell systems, whereas the presence of a heavy atom excessively complicates the solution of the many-determinant problem.

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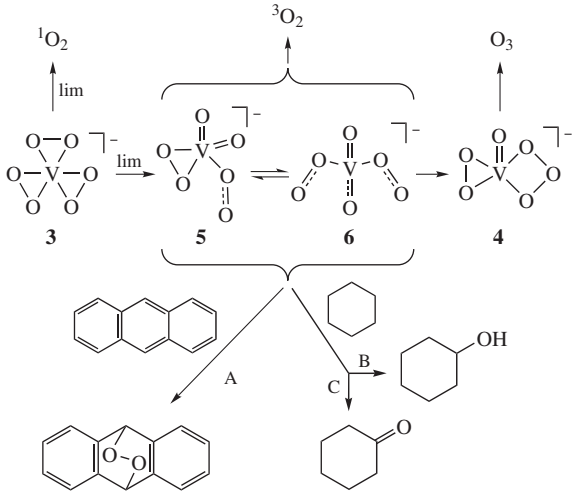


Scheme 2 Mutual conversions of vanadium complexes and routes for the formation of $^1O_2$, $^3O_2$ and O_3. Oxidation of anthracene and cyclohexane.

the triperoxo complex to reactive intermediates of oxidation of **5** and **6** suggests that this step can be slow, as also follows from kinetic experiments.[12] Evolution of singlet dioxygen from triperoxo complex **3**, which requires its significant inner-sphere reorganisation, also occurs slowly. On the other hand, intermediates **5** and **6** contain fragments that resemble coordinated singlet dioxygen and possibly play the role of its carriers to the substrate molecule. For a suitable acceptor of $^1O_2$, such as a substituted anthracene, this transfer according to Scheme 2 (route A) occurs quickly and does not limit the substrate oxidation.

One more feature of complex **6** is that only one of the two V–O oxo groups, namely, the axial group (1.600 Å), is a typical vanadyl group, whereas the other group (equatorial, 1.672 Å) is not equivalent to the first one, not only geometrically but also in other respects. It has been found for vanadyl groups in many peroxo and hydroperoxo complexes for which we made calculations that the V–O distance in the vanadyl group correlates linearly with the charge on the oxygen atom of this group,[†††] and that the charge on the oxygen atom decreases (becomes more negative) with an increase in the V–O interatomic distance (Figure 7). The charge of the O atom in the short V=O axial group in complex **6** fits in the correlation curve, whereas the charge on the O atom of the 'long' V–O group located in the equatorial plane is considerably higher than the correlation curve, hence it does not fit in the general trend for complexes of this type.

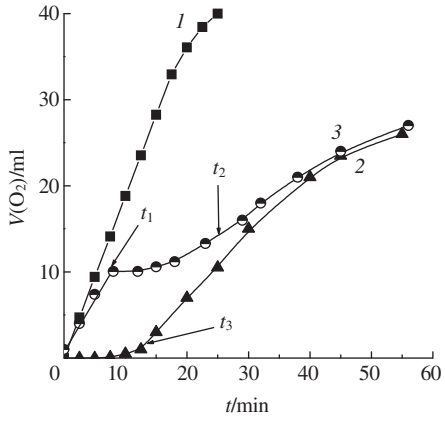


Figure 6 Amount of oxygen evolved in decomposition of hydrogen peroxide in the V^V/H_2O_2/AcOH system (*1*) in the absence of 2-ethylanthracene or (*2*) where 2-ethylanthracene is added at the start of H_2O_2 decomposition or (*3*) during H_2O_2 decomposition. $[H_2O_2] = 1$ mol dm^{-3}, $[V^V] = 10^{-4}$ mol dm^{-3}, [Substr] = 0.05 mol dm^{-3}, 50 °C.

[†††] B3LYP data.

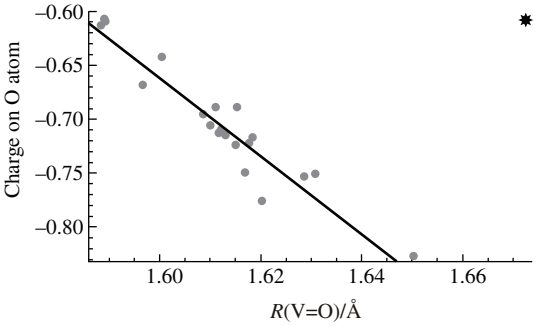
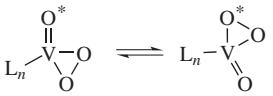


Figure 7 Correlation between the V–O bond length in the vanadyl group and the charge on the oxygen atom of this group. Asterisk denotes charge on the O atom of the 'long' V–O bond in complex **6**.

The small activation barrier of the **5** → **6** transition suggests that these complexes have a non-rigid structure. This non-rigidity is also indicated by the fact that decomposition of $H_2{}^{18}O_2$ in water in the presence of vanadium(V) compounds is accompanied with exchange of oxygen atoms between the peroxo ligand and the vanadyl group:[38]



When oxidation occurs in the V^V/H_2O_2/AcOH catalytic system, singlet dioxygen is transferred to an anthracene molecule and singlet oxygen is transferred to a cyclohexane molecule; in concurrent oxidation, cyclohexane and 2-ethylanthracene are consumed in parallel reactions;[39] *i.e.*, either both substrates react with the same reactive intermediate, or different reactive intermediates are responsible for the transfer of singlet dioxygen and a singlet oxygen atom, but transition between them occurs with a small activation energy and hence occurs quickly.

Intermediates **5** and **6**, the existence and structure of which were revealed by quantum-chemical calculations, well match both of the suggested mechanisms. In fact, according to calculations, these complexes should readily undergo conversion into each other (Figure 2). It can be assumed that both intermediates can transfer singlet dioxygen to the substrate.

It is yet too early to discuss the detailed mechanism of interaction of such complexes with cyclohexane and linear or branched alkanes. However, one can suppose within the available kinetic data that complexes **5** and **6** may be good donors of a singlet oxygen atom, which results in the formation of cyclohexanol from cyclohexane and nitrous oxide from nitrogen. Similarly, the transfer of the O^+ cation from these complexes to cyclohexane should give cyclohexanone and the reaction with alkanes should result in cleavage of a C–C bond.

In conclusion, the quantum-chemical simulation of the structure and inner-sphere reactions of peroxo complexes with the general formula $[VO_6]^-$ revealed a number of important features that could not be assumed *a priori* or established by other methods. Probably, the main result is the conclusion on the structural non-rigidity of the closest environment in 'oxygen-excessive' vanadium complexes with d^0 configuration. The earlier hypothesis on the existence of complexes with a coordinated O_3 ligand has been confirmed.

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