Mendeleev Commun., 2004, 14(3), 117–118

Is nitrous oxide an intermediate product in the oxidation of molecular nitrogen by vanadium peroxo complexes?

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DOI: 10.1070/MC2004v014n03ABEH001829

According to the B3LYP calculations, nitrous oxide, the product of N_2 oxidation by peroxo vanadium complexes, easily adds to the V=O bond to form hyponitrite, which undergoes further oxidation.

Previously,[1] nitrogen fixation was analysed, and it was concluded that oxygen atom transfer from the peroxo ligand of metal complexes to the nitrogen molecule possesses a low activation barrier. The conclusion corresponds to the experimental observation of N_2O formation from nitrogen in the $V^V/H_2O_2/CF_3COOH$ system[2] at room temperature and even below it. Molecular nitrogen oxidation by hydrogen peroxide is thermodynamically favourable:

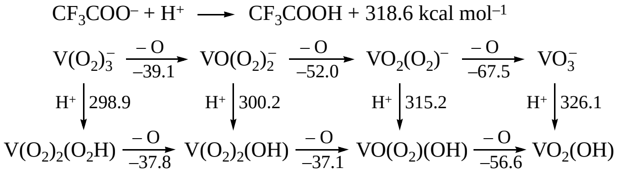
$$H_2O_2(l) + N_2(g) \rightarrow H_2O(l) + N_2O(g),\ \Delta G^0_{f,298} = -13.1\ \text{kJ mol}^{-1}.$$

In the vanadium(V)-catalysed reaction, nitrous oxide is formed fast enough but its quantity is small,[2] in spite of the possibility to achieve high equilibrium concentrations of N_2O. The further deep oxidation of N_2 to nitric acid, for instance, results in the greater gain of free energy. Therefore, there is a question, how easily the nitrous oxide to be oxidised further on, and we theoretically studied N_2 oxidation to N_2O and further under the action of various vanadium peroxo complexes. For all complexes, only one type of initial reactions of O atom transfer from the O_2 ligand to N_2 was considered.

The calculations were carried out with the B3LYP hybrid density functional method using the GAUSSIAN 98 program.[3] The optimisation of the geometry of the stationary states was done in the 6-31G* basis. The type of the obtained structure was confirmed by frequencies analysis in a harmonic approximation. Then, the total energy of the system was calculated in the extended 6-311++(*d,p*) basis taking into account a zero point energy in the B3LYP/6-31G* approximation.

It is known that vanadium(V) peroxo complexes may include different numbers of peroxo groups.[4–9] Thus, the reactivities of mono-, di- and triperoxo complexes, $[V(O_2)_n(O)_{3-n}]^-$ (n = 1–3), as well as of the protonated forms $[HV(O_2)_nO_{3-n}]$, were studied. For the $[V(O_2)_3]^-$ complex, the D_3 symmetrical structure with d(O–O) = 1.475 Å and d(V–O) = 1.819 Å, and the C_{2v} structure with two different peroxo ligands (the result of D_3 structure relaxation after rotation of one O_2 ligand around the C_2 axis): d(O–O) = 1.455 Å, d(V–O) = 1.850 Å; 1.794 Å and d(O–O) = = 1.470 Å, d(V–O) = 1.916; 1.754 Å, have close energies. The first is higher in the 6–31G* basis and is lower in the 6-311++G** basis. Since the corresponding transition state of O-atom transfer has approximate C_{2v} symmetry, it is directly connected with the low-symmetry $[V(O_2)_3]^-$ structure.

In the case of n = 1, 2, only the protonation of the oxo group was considered. The protonation of a triperoxo complex (n = 3) has a unique result of hydroperoxo group formation. It has bidentate coordination with one elongated V–O bond [Figure 1(*a*)]. The same HO_2 coordination mode was found previously for protonated peroxo complexes of vanadium.[10–12] The protonation at the O_2 site is slightly more favourable than that at the O site. A comparison of the heats of protonation for $[V(O_2)_n(O)_{3-n}]^-$ (n = 1–3) complexes[†] (Scheme 1) and the calculated heat of protonation for the trifluoroacetate anion, equal to 318.6 kcal mol^{-1}, demonstrates that only a vanadium monoperoxo complex and, in a smaller degree, a vanadium diperoxocomplex can exist in the protonated form in trifluoroacetic acid.



Scheme 1

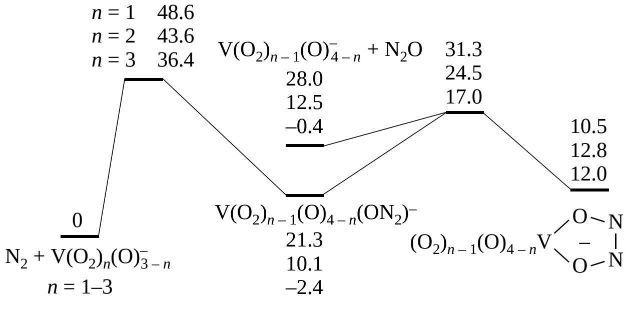
A comparison of the binding energies of an O atom in the peroxo group and N_2–O bond energy in nitrous oxide 39.5 (calculated) or 39 kcal mol^{-1} (experimental) shows that only for triperoxo complexes and protonated diperoxo complexes oxygen transfer to the nitrogen molecule is a practically thermoneutral process. In the other cases, the energy loss varies from 13 to 28 kcal mol^{-1}.

Schemes 2 and 3 demonstrate the energy diagrams for oxygen atom transfer from vanadium peroxo complexes to the nitrogen molecule.

It can be seen that the activation energy of nitrous oxide formation is regularly reduced in the order of mono-, di- and triperoxo complexes of vanadium. At the protonation there is an additional decrease of activation energy, and the lowest activation energy equal to 30.7 kcal mol^{-1} occurred in the $[V(O_2)_2(OH)]$ complex [Figure 1(*b*)]. Thus, protonated diperoxo complexes display the greatest reactivity towards molecular nitrogen oxidation.

The binding energy of N_2O in products, $[V(O_2)_{n-1}O_{3-n}(ON_2)]^-$, is small. For neutral $[HV(O_2)_{n-1}O_{3-n}(ON_2)]$ complexes [Figure 1(*c*)], it is 16 kcal mol^{-1}.[‡] Therefore, all these complexes will easily release N_2O. However, the addition of a N_2O molecule to a double V=O bond with formation of hyponitrites [Figure 1(*d*),(*e*)] competes with this process. The corresponding activation barriers are small (from 3 to 17 kcal mol^{-1} in the initial anionic complexes), and they are higher (from 10 to 25 kcal mol^{-1}) in the neutral protonated complexes. Note that the formation of *cis*-hyponitrites from N_2O and oxides was observed experimentally.[13]

Neutral hyponitrites, as a rule, are formed with rather high energy consumption and have rather low barriers, no more than 6 kcal mol^{-1}, for the reverse transformation into initial complexes of nitrous oxide. Therefore, their equilibrium concentration will



Scheme 2

[†] The similar protonation heats were obtained in RHF/6-311++G(*d,p*) approach, 320.2, 300.8 and 320.2 kcal mol^{-1},[11] for n = 1, 2 and 3, respectively.

[‡] The N_2O binding energy for the hydroxy $[V(O_2)_2(OH)(ON_2)]$ complex, 6.8 kcal mol^{-1}, is close to the corresponding value for an analogous complex in the case of n = 2.

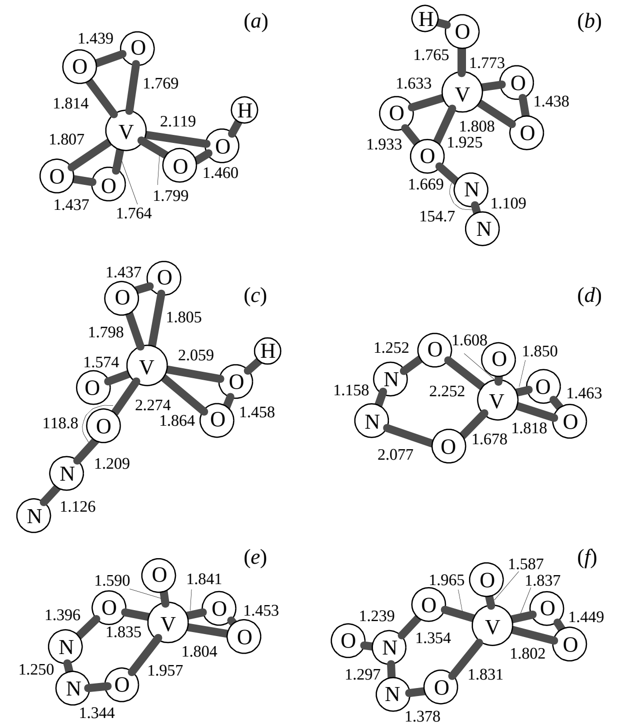
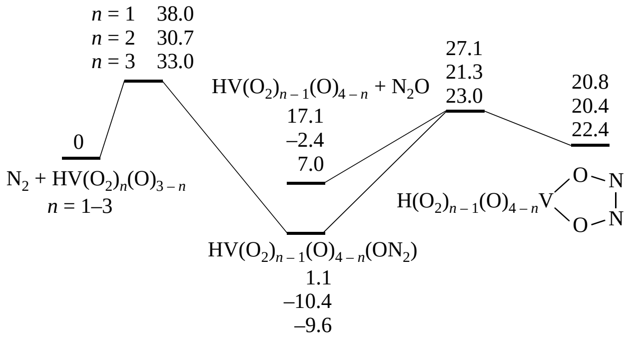


Figure 1 The calculated structures of (*a*) the peroxo complex $[V(O_2)_2(O_2H)]$, (*b*) the transition state in the reaction $[V(O_2)_2(OH)] + N_2 \rightarrow [V(O_2)(O)(OH)(ON_2)]$, (*c*) the hyponitrite complex $[V(O_2)_2(ONNO)]^-$, (*d*) the nitrous oxide complex $[V(O_2)(O)(O_2H)(ONN)]$, (*e*) the transition state in the reaction $[V(O_2)(O)_2(ON_2)]^- \rightarrow [V(O_2)(O)(ONNO)]^-$, (*f*) the trioxodinitrate complex $[V(O_2)_2(O_2NNO)]^-$. The bond lengths are in Å and angles are in degrees.

be negligibly small. Oppositely, the negatively charged hyponitrite complexes are more stable, and the high equilibrium concentrations are achievable for them. According to the present calculations, hyponitrous ligands in the complexes have an evident affinity to the oxygen atom of 63.7±0.7 kcal mol^{-1} for $n = 1$–3. Thus, the majority of peroxo complexes in the system (see V–O dissociation energies in Scheme 1) can oxidise hyponitrites to trioxodinitrates [Figure 1(*e*)] with the energy gain up to 25 kcal mol^{-1}. Because of a known correlation of the kinetic and thermodynamic characteristics of related reactions,[14] it is possible to believe that activation barriers for further oxidation of hyponitrites are much lower than those found for molecular nitrogen oxidation. This creates a possibility for deep oxidation of nitrogen by vanadium peroxo complexes to form nitric acid.



Scheme 3

Thus, on the basis of the B3LYP calculations, under the interaction of N_2 with vanadium(V) peroxo complexes the following processes are expectable. The protonation of $[V(O)(O_2)_2]^-$ diperoxo complex results in the appearance of the active form $[V(O_2)_2(OH)]$, which is capable to oxidise nitrogen to nitrous oxide. The reaction product, a complex of nitrous oxide, can decompose with the release of N_2O into the solution, or it can be deprotonated. In this case, there is a low activation barrier for nitrous oxide transformation into a hyponitrite ligand, which can be easily oxidised to trioxodinitrate and, finally, to nitrate.

This work was supported by the Russian Foundation for Basic Research (grant no. 01-03-33076).

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Received: 11th July 2003; Com. 03/2155