# 산소에 의한 바나듐(III) 이온의 산화반응에 대한 O¹⁸ 동위원소 연구*

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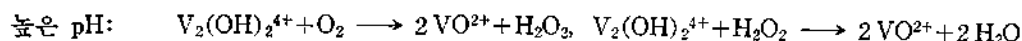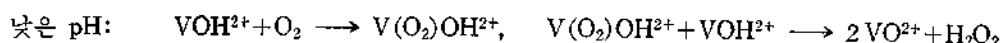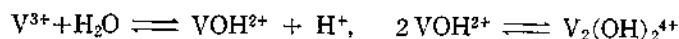# Tracer Study Using H₂O¹⁸ on the Oxidation of Vanadium(III) by Molecular Oxygen*

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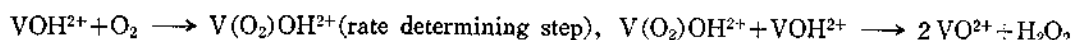***Department of Chemistry, Korea University, Seoul, Korea

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요 약. 과염소산 수용액 중에서 바나듐(III)이온이 산소에 의해 산화되는 반응에 대해서 pH 범위 1~3에 걸쳐 H₂O¹⁸을 이용한 동위원소 실험을 행했다. 반응속도식 $-\dfrac{d[V(III)]}{dt}=k_1\dfrac{[O_2][V(III)]}{[H^+]}$ 가 성립되는 높은 히드로늄이온 농도(pH<~2)에서는 반응생성물 VO²⁺ 이온의 산소가 모두 산소분자에서 유래된다는 결과를 얻었다. 반면 $-\dfrac{d[V(III)]}{dt}=k_2\dfrac{[O_2][V(III)]^2}{[Ht]^2}$ 의 속도식이 성립하는 pH >~2 범위에서의 추적자 실험은 바나딜이온의 산소의 50%가 산소분자에서 온다는 결과를 주었다. 반응속도론의 결과 화학량론적 결정과 아울러 동위원소 실험결과를 고려하면 다음과 같은 반응 메카니즘을 제안할 수 있다.

$$V^{3+}+H_2O \rightleftharpoons VOH^{2+} + H^+, \quad 2\,VOH^{2+} \rightleftharpoons V_2(OH)_2^{4+}$$

낮은 pH:    $VOH^{2+}+O_2 \longrightarrow V(O_2)OH^{2+}, \quad V(O_2)OH^{2+}+VOH^{2+} \longrightarrow 2\,VO^{2+}+H_2O_2$

높은 pH:    $V_2(OH)_2^{4+}+O_2 \longrightarrow 2\,VO^{2+}+H_2O_3, \quad V_2(OH)_2^{4+}+H_2O_2 \longrightarrow 2\,VO^{2+}+2\,H_2O$

**Abstract.** Isotopic experiments using H₂O¹⁸ on the oxidation of V(III) in acid perchlorate by molecular oxygen were performed in the range pH 1.0 to 3.0. At pH<2, where a rate equation of the form $-\dfrac{d[V(III)]}{dt}=k_1\dfrac{[O_2][V(III)]}{[H^+]}$ is adequate, the tracer study clearly indicated that all the product vanadyl ion's (VO²⁺) oxygen originated from the molecular oxygen. At pH>~2, where a different rate expression of the form $-\dfrac{d[V(III)]}{dt}=k_2[O_2]\dfrac{[V(III)]^2}{[H^+]^2}$ is required, the isotopic experiment showed that half the vanadyl oxygen originated from the molecular oxygen.

Considering the results of the isotopic study, a mechanism for the V(III)-O₂ reaction at pH<~2 may be suggested as follows:

$$VOH^{2+}+O_2 \longrightarrow V(O_2)OH^{2+}(\text{rate determining step}), \quad V(O_2)OH^{2+}+VOH^{2+} \longrightarrow 2\,VO^{2+}+H_2O_2$$

The tracer results at pH>~2 imply that the rate determining step may be

$$V_2(OH)_2^{4+}+O_2 \longrightarrow 2\,VO^{2+}+H_2O_2$$

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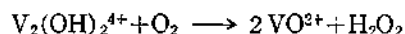
* Experiments Performed at the University of Virginia, Charlottesville, Va., U.S.A.

followed by    $V_2(OH)_2{}^{4+}+H_2O_2 \longrightarrow 2\,VO^{2+}+2\,H_2O$

after establishing the equilibria

$$V^{3+}+H_2O \rightleftharpoons VOH^{2+}+H^+, \text{ and } 2\,VOH^{2+} \rightleftharpoons V_2(OH)_2{}^{4+}$$
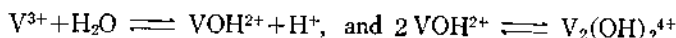
## Experimental

**The Exchange of Vanadyl Oxygen and Water.** One of the conditions for the success of the tracer experiment using $H_2O^{18}$ in the oxidation of vanadium (III) by molecular oxygen is that the exchange between the product vanadyl oxygen and solvent water must be slow relative to the oxidation of vanadium (III). Otherwise, the isotopic ratio of $O^{18}/O^{16}$ of vanadyl ion obtained from the oxidation of vanadium (III) would not give any significant clue to the oxidation mechanism of vanadium (III) by molecular oxygen. Therefore, the exchange reaction of oxygen between vanadyl ion and water should be studied preparatory to performing oxygen tracer studies on the oxidation of vanadium (III) in perchloric acid, although it is expected to be very slow in view of the fact that the $VO^{2+}$ species is known as one of the most stable and persistent diatomic cations[1]. The determination of isotopic composition of oxygen in inorganic compounds is usually based on a procedure in which solvent was sampled for isotopic analysis[2]. Namely, a small amount of the solution under consideration was distilled on a vaccum line and the distilled water was then equilibriated with an appropriate amount of dry carbon dioxide gas[3]. The %$O^{18}$ in the water was then calculated from the equilibrium

$$C^{12}O_2{}^{16}+H_2O^{18} \rightleftharpoons C^{12}O^{16}O^{18}+H_2O^{16}$$
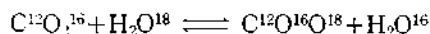
with the equilibrium constant of 2.078[4] at 25°C. It usually took several days to reach the complete equilibrium.

However, in this work a method of direct sampling of the vanadyl ion was used similar to that used in the case of uranyl oxygen–water[5] and plutonyl oxygen–water system[6]. Mercuric cloride was used as the reagent[7] and the carbon dioxide formed was analyzed by mass spectrometry to obtain the isotopic ratio, $O^{18}/O^{16}$, of the vanadyl ion. It was found that vanadyl ion forms a brown precipitate with an aqueous solution of potassium ferrocyanide. Potentiometric study performed on V(IV)—potassium ferrocyanide reaction[8] suggested that addition of $K_4Fe(CN)_6$ solution to aqueous $VOSO_4$ solution yielded the compound $K_2(VO^{2+})_3[Fe(CN)_6]_2$. The detailed procedure for determining the isotopic composition of the vanadyl ion was as follows: The stock solution of $VO^{2+}$ in perchloric acid was diluted with $O^{18}$—enriched water. The oxygen—18 content of the solvent was analyzed immediately by the following method[7]: 100mg of analytical 1:1 mixture of $HgCl_2$ and $Hg(CN)_2$ were introduced into a pyrex glass vessel with a stop-cock serving as a seal-off construction and the mixture of $HgCl_2$—$Hg(CN)_2$ was rigorously dried under vacuum line. A small amount of the water sample was then introduced into the reagent mixture on the vacuum line by condensing water distilled from the vanadyl solution. In this experiment a large excess of water sample was taken in order to avoid any significant error caused by the moisture getting into any of the reagents involved or into the vessel. The sample tube containing $HgCl_2$—$Hg(CN)_2$ mixture and water sample was evaluated to about $10^{-3}$ mmHg and sealed off under vacuum. Next it was heated to.

400°C for two hours. The sample tube was opened on the vacuum line and the gaseous products were condensed by use of liquid nitrogen into a second degassed vessel. The non-condensable gases formed, nitrogen and carbon monoxide, were pumped off. It should be noted that the formation of carbon monoxide which is a loss of oxygen for analysis increases with temperature. Gaseous cyanogen is formed as a by-product in this procedure and hydrogen chloride is formed as well in analyzing water samples. Both of these by-products can be separated from the carbon dioxide by reaction with amalgamated zinc at 200 °C[7]. For water analysis mercuric cyanide was used in order to provide carbon atoms for the formation of carbon dioxide. It has been shown that this method of obtaining carbon dioxide from inorganic oxygen-containing compounds failed to give any $CO_2$ with dry silicates[7]. Therefore, the reaction was carried out in glass vessels without risk of isotopic dilution. The isotopic composition of $CO_2$ was obtained by the measurement of the isotope mass ratio $46/(45+44)$ with a mass spectrometer.

The vanadyl solution was prepared under the condition where $[VO^{2+}] = 0.185 M$, $[H^+] = 0.2 M$ and an ionic strength of 1 moral using lithium perchlorate, and the solution was kept in a thermostat at 25°C. The exchange of oxygen between vanadyl ion and solvent water was followed by analyzing the isotopic composition of carbon dioxide formed from the vanadyl ion. Aliquots of 0.1 m mole of vanadyl ion in oxygen—18 enriched water were removed as a function of time and the exchange reaction was quenched by the addition of 0.05 m mole of aqueous potassium ferrocyanide with rapid stirring. Thirty milliliters of acetone was added to aid filtration and the brown precipitate was collected on a sintered glass filter and dried by

pumping for an hour on a vacuum line. The dark brown solid was introduced into the sample tube containing 50 mg of analytical, vacuum dried, anhydrous $HgCl_2$;no $Hg(CN)_2$ was added to these samples since ferrocyanide ions provide the source of carbon atoms for the formation of carbon dioxide. The sample tube was evacuated to less than $10^{-3}$ mmHg. The rest of the steps were the same as those for the $H_2O$ analysis described previously. The mass spectrometer reading were calibrated using $CO_2$ samples of known enrichment in order to reduce possible error due to instrumental variations. The only oxyanion added to the vanadyl solution was perchlorate ion and it should be tested whether the data were affected by the exchange of the perchlorate with water. The kinetics of the isotopic exchange reaction between perchlorate ion and water have been measured.[9] The results showed that the perchlorate ion does not measurably exchange its oxygen with water over long periods of time at elevated temperatures and high acidities. In $9 M$ perchloric acid at room temperature, the half-life for exchange was estimated to be greater than one hundred years.

For comparison, the results for analysis of water samples by the $HgCl_2$—$Hg(CN)_2$ method are tabulated in *Table* 1 with those of the $CO_2$ equilibrium method mentioned earlier[7]. Changing the amount of water in a sample by

*Table* 1. Comparison of $HgCl_2$—$Hg(CN)_2$ method and $CO_2$ equilibrium method

| Amount of $H_2O$ mg | % $O^{18}$ by $HgCl_2$—$Hg(CN)_2$ method | % $O^{18}$ by $CO_2$ equilibrium method |
|---|---|---|
| 4 | 4.12 | 3.97 |
| 4 | 4.21 | 4.25 |
| 3 | 9.21 | 9.43 |
| 200 | 9.39 | 9.40 |
| 200 | 22.1 | 21.9 |

a factor of fifty or more has no significant effect on the results of analysis, however, 3~4 mg samples show lower results due to isotopic dilution.

**Tracer Experiments Using Oxygen-18(On the Oxidation of Vanadium (III) by Molecular Oxygen)**

Meaningful tracer experiments can be done if the product vanadyl ion does not exchange rapidly with solvent water oxygen or with the oxidizing agent, $O_2$, and the oxygen molecule does not induce exchange of vanadyl oxygen with the solvent. The steps for carrying out a tracer experiment on the oxidation of vanadium (III) by molecular oxygen were as follows: preparation of vanadium (III) perchlorate solution in oxygen-18 enriched water; analysis of the solvent for the isotope ratio of $O^{18}/O^{16}$; passing an oxygen stream through the solution to bring about reaction; precipitation of the vanadyl ion with ferrocyanide; conversion of oxygen in the vanadyl ion to carbon dioxide; mass spectrometric analysis of the carbon dioxide.

All the steps involved were essentially the same as those described previously in the exchange reaction of vanadyl oxygen and water. It should be mentioned that an excess of ferrocyanide was avoided to prevent contamination by solvent water.

**Results**

**The Exchange Reaction between the Vanadyl Oxygen and Water.** The exchange reaction betweeen $VO^{2+}$ and $H_2O$ was studied at 25°C and the results are given in *Table* 2. Figure 14 shows a linear McKay plot[10] for the vanadyl oxygen-water exchange with a 0.185 $M$ solution of unlabeled $VO^{2+}$ in 0.2 $M$ perchloric acid at an ionic strength of 1.0. The sample was prepared in 5 atom % oxygen—18

enriched water.

It has been reported that the vanadyl ion may be protonated under certain conditions,[11] although this conclusion has been criticized.[12]

The equilibrium constant for the hydrolysis step

$$VO^{2+}+H_2O \rightleftharpoons VO(OH)^+ + H^+$$

is given[18] by

$$\frac{[VO(OH)^+][H^+]}{[VO^{2+}]} = 10^{-6.0}$$

Since it is possible that the exchange of oxygen between vanadyl ion and water takes place through the hydrolyzed species $VO(OH)^+$, it seems worthwhile to follow the exchange reaction under the condition that the hydrolyzed vanadyl ion is dominant.

The effect of acidity on the rate of the exchange reaction was thus studied qualitatively as follows: to the resulting solution obtained from the above exchange experiment was added $NaHCO_3$ to the extent that the color of the solution started to change from aqueous vanadyl blue to dark-blue of the hydrolyzed species. The sample was kept in a temperature bath at 25°C for 144 hours. The percentage of exchange during the time interval was 31.4 %. Since the sample was originally exchanged by 6.7%,

*Table* 2. Rate of exchange of vanadyl oxygen and water. $[VO^{2+}]=0.185\,M$, $[H^+]=0.2\,M$, Temp. $=25°C$, $\mu=1\,M$ (LiClO$_4$)

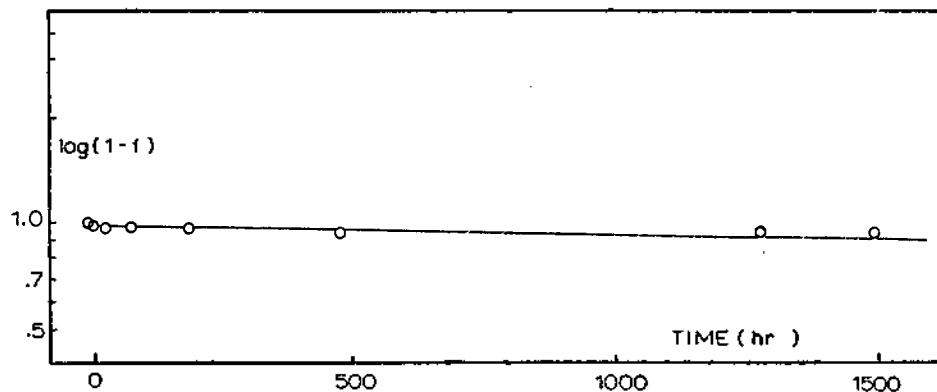| Exchange time hr. | 46/(44+45) mass ratio | % Exchange | $(1-f)$ |
|---|---|---|---|
| 0 | .220 | 0 | 1.0 |
| 20 | .400 | 4.09 | .959 |
| 70 | .255 | .80 | .992 |
| 185 | .370 | 3.6 | .964 |
| 472 | .550 | 7.5 | .925 |
| 1266 | .500 | 6.4 | .936 |
| 1485 | .515 | 6.7 | .933 |
| ∞ | 4.62 | 100 | 0 |

*Fig.* 1. The McKay plot of the exchange of vanadyl oxygen and water

the net exchange during the reaction interval of 144 hours at the higher pH was calculated to be $31.4-6.7=24.7\%$. Although it is admittedly crude, the result seems to indicate that the exchange reaction is inversely proportional to hydrogen ion concentration. It should be pointed out, however, that the dark blue solution of V(IV) at higher pH undergoes further color change to yellow-tinged blue and finally precipitation, on standing for several days.

The half-life for the exchange reaction between the vanadyl oxygen and water was determined by the following relation derived from the McKay equation[10], where $f$ is the fraction of sample which has exchanged.

$$t_{1/2}=\frac{.301\times t}{\log(1-f)}=\frac{.301\times 1485}{\log .93}$$

$$=1.42\times 10^4 \quad (\text{hr})$$

Although there is some scattering in the seven individual points, the half-life of the exchange reaction was calculated from the slope of the linear McKay plot. The result indicated that the half-life lies in the order of $10^4$ under the experimental condition.

**Oxygen—18 Tracer Studies on the V(III)—O$_2$ Reaction**

(*a*) **High Acidities (pH<2)**. The extent of oxygen transferred from the oxidizing agent,

i.e., molecular oxygen, was determined under experimental condition such that $[V(III)]=.067$ $M$, $[H^+]=.047 M$ and $\mu=1.3(\text{LiClO}_4)$. The percentages of exchanges of obtained were .7 %, .5 %, .49 % and .42 % with 4.43 % oxygen—18 enriched solvent. The number of oxygen atoms per vanadyl ion derived from oxidizing agent was calculated by the following equation[14]:

$$n=\frac{R_{H_2O}-R_{VO^{2+}}}{R_{H_2O}-R_{O_2}}$$

where $R$ refers to the experimentally determined ratio of $O^{18}/O^{16}$ in the solvent or vanadyl ion or oxygen molecule. Thus, the number of oxygen atoms in the product which originated from the oxygen molecule are calculated to be .89, .93, .94 and .95, the average being .94. Considering the slow exchange of the product of the autoxidation, vanadyl ion, with the solvent and the side reaction between V(III) and $ClO_4^-$ ion[19], it seems reasonable to conclude that under these conditions all the oxygen in the vanadyl ion is essentially transferred from the oxidizing agent, molecular oxygen and none from the water solvent.

(*b*) **Low Acidities (pH>2)**. Tracer experiments on the V(III)—O$_2$ system were performed

under the experimental condition where the stoichiometry of the $V(III)/O_2$ reaction was determined to be 4/1. The autoxidation was carried out such that $[V(III)] = .043 M$, pH= 2.4 with no added salt. The solvent analysis showed that the ratio $O^{18}/O^{16}$ of water was 4. 71 % by averaging five values. The $O^{18}/O^{16}$ ratio obtained with the product vanadyl ion was averaged from five values to be 2.44 %. Therefore, the number of oxygen atoms derived from molecular oxygen at high pH is calculated to be

$$n = \frac{R_{H_2O} - R_{VO^{2+}}}{R_{H_2O} - R_{O_2}} = \frac{4.71 - 2.44}{4.71 - .22} = .505$$

The value of $n = .5$ suggests that half of the product's oxygen atoms are derived from the oxygen molecule while the other half is transferred from the solvent water.

As mentioned in the experimental section, the isotope ratio reading with the mass spectrometer varied depending on small instrumental variations. The standard deviation was determined by reading the standard sample on five consecutive days. The deviation was calculated to be $\pm 7.1$ %.

## Discussion

This investigation has a concern for the question: Does the autoxidation of the transition metal ion take place via one-electron or two-electron steps?[16,17]

Prior to the tracer study using $H_2O^{18}$ on the $V(III) - O_2$ reaction, the exchange of $VO^{2+}$ with $H_2O$ was studied and found to be very slow with a half-life of $\sim 10^4$ hours.

Since the over-all reaction at low pH involves the side-reaction of $V(III)$ with perchlorate ion, one must consider the effect of the side-reaction on the tracer study. The over-all V (III) —perchlorate reaction[18] may be represented by

$$8V^{3+} + ClO_4^- + 4H_2O \longrightarrow 8VO^{2+} + Cl^- + 8H^+$$

The rate constant was approximately resolved into two terms such as
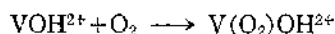
$$k_3 = k_3' + k_3'' [H^+]$$

for the rate expression

$$-\frac{d[V(III)]}{dt} = k_3 [V^{3+}] [ClO_4^-]$$

The above mechanism suggests that a maximum of half of the oxygen atoms in the vanadyl ion originated from the water oxygen and the other half from the perchlorate oxygen. Therefore, in addition to the slow exchange of vanadyl oxygen with water, the oxidation by perchlorate ion, if any, would give a higher result in the tracer experiment for the $V(III) - O_2$ reaction in perchlorate solution.

At $pH < \sim 2$, the stoichiometry of $V(III)/O_2$ was determined to be 2 and hydrogen peroxide was detected during the reaction. Based also on the kinetic results, the following mechanism may be suggested to fulfill the requirement that all the oxygen in the vanadyl ion is transferred from the oxidizing agent, molecular oxygen.

$$VOH^{2+} + O_2 \longrightarrow V(O_2)OH^{2+}$$
$$\text{rate determining step}$$
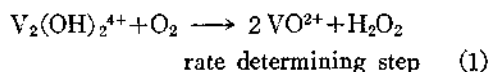$$V(O_2)OH^{2+} + VOH^{2+} \longrightarrow 2 VO^{2+} + H_2O_2$$
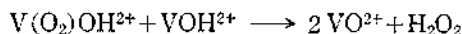
In other words, the reaction of the metal ion with hydrogen peroxide may be disregarded under the experimental condition of $pH < \sim 2$.
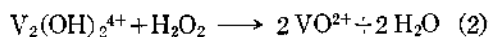
The rate determining step is the complex formation between the hydrolyzed metal ion and the oxygen molecule, although there is no evidence regarding the electronic structure of the complex to conclude whether or not two-electron transfer takes place in the complex $V(O_2)OH^{2+}$. In other words, the oxygenated complex may involve either an $O_2^{2-}$ peroxide linkage or an $O_2^-$ superoxide group. In the

transition state the oxygen molecule would either the first coordination sphere of the hydrolyzed metal ion and then electron transfer would take place to the oxygen molecule via an intramolecular redox process. Thus it seems likely that the autoxidation of V(III) takes place by way of an inner-sphere mechanism, rather than by an outer-sphere mechanism in which no penetration of the first coordination sphere of metal ion by the oxidizing agent occurs. The first resulting species will be formally $V(O_2^-)OH^{2+}$. However, since the electron affinity of the oxygen is not yet saturated, it is possible for the oxygen in $V(O_2^-)OH^{2+}$ to accept another electron to form the peroxide state $(O_2^{2-})$. Whether the second transfer occurs in practice would depend on the charge density already present on the $O_2^-$ group, that is, on the other ligands attached to the vanadium atom. Many metal cations have two valence states suitable for charge transfer with oxygen. However, even if the relative thermodynamic energies and kinetic reactivities favor formation of 1:1 adducts with oxygen, most of these species must be too unstable with regard to side reactions to allow detection. If the electron density on the oxygen is too high, then the addition of a second cation may be prohibited so that the binuclear species containing an $O_2^{2-}$ bridge may not be formed. In practice a number of 1:1 adducts are known but very few $O_2$-bridged binuclear complexes of metal ions other than cobalt have been reported. Most of these have not yet been studied sufficiently to confirm the structure. One such system is known between atomic lithium or sodium and molecular oxygen.[20] In contrast to the rare binuclear complexes with peroxo bridges, numerous hydroxo bridged complexes of metal cations other than cobalt are reported for Co(III), Fe(III), Cr(III) and V(III).
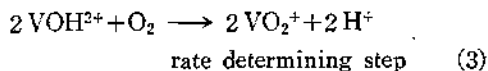
The stoichiometry of the reaction at pH>2 was found to be $V(III)/O_2=4$ and the isotopic experiments showed that half of the oxygen atoms were transferred from the oxygen and the other half from the labeled water. Furthermore, the kinetic results that the rate at pH >~2 is proportional to the second power of metal ion and inversely proportional to the second power of hydrogen ion concentration imply that the rate-determining step at pH>~2 may be either
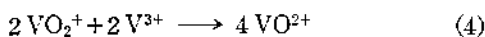
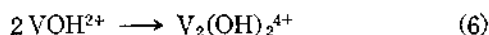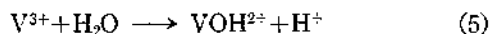$$V_2(OH)_2^{4+}+O_2 \longrightarrow 2VO^{2+}+H_2O_2$$
$$\text{rate determining step} \quad (1)$$

followed by

$$V_2(OH)_2^{4+}+H_2O_2 \longrightarrow 2VO^{2+}+2H_2O \quad (2)$$

or

$$2VOH^{2+}+O_2 \longrightarrow 2VO_2^++2H^+$$
$$\text{rate determining step} \quad (3)$$

followed by

$$2VO_2^++2V^{3+} \longrightarrow 4VO^{2+} \quad (4)$$

after establishing the epuilibria

$$V^{3+}+H_2O \longrightarrow VOH^{2+}+H^+ \quad (5)$$

$$2VOH^{2+} \longrightarrow V_2(OH)_2^{4+} \quad (6)$$

The suggested transition state of the reaction at pH>2 may be written in both equations (1) and (3) as
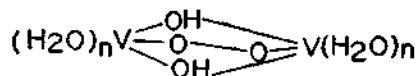


whereas, the transition state at pH<~2 is a complex between $VOH^{2+}$ and oxygen.

Although binuclear complexes having more than one bridge of the same kind are rare, it is an exception with the hydroxo bridged species. The geometry of binuclear complexes

having one, two, or three bridging groups can be visualized as two octahedra sharing a corner, edge or face, respectively. The single bridged peroxo complexes are important as intermediates in the preparation of other dicobaltic complexes and, on the biological side, as models of oxygen carriers.

The oxidation at $pH > \sim 2$ can be described in terms of either a 2-electron transfer expressed in equation (1) or 4-electron change shown in equation(3). However, there seems to be no experimental evidence that would serve as a basis for discrimination between these two mechanisms. The negative result for $H_2O_2$ detection can be applied to either case, since fast reaction of $H_2O_2$ with $V_2(OH)_2^{4+}$ will give a negative test for $H_2O_2$.

It is reported that $VO_2^+$ ion reacts rapidly with V(III) in accordance with the following rate expression:[21]

$$-\frac{d[V(V)]}{dt} = k'[V(III)][V(V)]$$

where $k'$ is given by

$$k' = k_{-2}[H^+]^{-2} + k_{-1}[H^+]^{-1} + k_0 - k_1[H^+].$$

Therefore, the intermediate $VO_2^+$ in equation (3) can not be identified to prove that the step (3) actually takes place in the course of the reaction.

As mentioned earlier, the reaction path (3) involves an almost synchronous 4-electron reduction of molecular oxygen, however, it is known[17] to be possible only in oxidations by enzyme where a substrate has a specifically[1] fixed steric position.

Considering the above factors, it may well be said that the major reaction at $pH > 2$ takes place through two 2-electron change as shown in equations (1) and (2).

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