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Oxygenation of Vanadyl(IV). Effect of Coordinated Surface Hydroxyl Groups and OH⁻

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The oxygenation kinetics of vanadyl in solution and in the presence of δ -Al₂O₃ and TiO₂ (anatase) was investigated as a function of pH, p_{O_2} , temperature, and surface area concentrations. In the presence of the hydrous oxides the oxidation reaction is preceded by specific adsorption, characterized and measured in terms of formation of surface complexes: $2(=MOH) + VO^{2+} \rightleftharpoons VO(OM=)_2 + 2H^+$. The rate laws can be interpreted in terms of a rate dependence on the concentrations of dissolved oxygen and the concentrations of $VO(OH)^+$ in the homogeneous solution and on that of V(IV) bound to the hydrous oxide surface, $VO(OM=)_2$, in the heterogeneous system, respectively. The kinetic interpretation given is in line with an inner-sphere nature of the surface complex. The rate constants (25 °C, M⁻¹ s⁻¹) are 1.07, 0.051, and 0.028, respectively, for the homogeneous system, in the presence of TiO₂ and Al₂O₃. These results are compared with published data on the oxygenation of Fe(II) and Mn(II) to illustrate more generally that complex formation with surface hydroxyl groups produces similar kinetic effects on the oxygenation as complex formation with OH⁻ in solution.

Introduction

Oxygenation of transition-metal ions is a subject of considerable interest in geochemistry,¹ corrosion, and technical applications. The electron transfer in aqueous media occurs either homogeneously or at surfaces. It has long been known that hydroxo complexes of metal ions like Fe(II),² Ti(III),³ V(III),⁴ and U(IV)⁵ are oxidized faster by oxygen than by the corresponding aquo ion; early mechanistic interpretations on the effect of hydrolysis were outlined by Fallab.⁶ It was shown recently that adsorption at oxide surfaces can accelerate oxygenation of Fe(II)⁷ and Mn(II)⁸ in a manner similar to hydrolysis. It thus appears that the specific adsorptive interaction of a metal ion with the surface hydroxo groups of a hydrous oxide surface can have similar effects on oxygenation as hydroxo complex formation in solution.

As a consequence, oxidation by dissolved oxygen of hydrolyzed and adsorbed metal ions may often be parallel processes, especially if the reactant is readily adsorbed; often the oxygenation products are insoluble, as in the case of Fe(II) and Mn(II), and may act "autocatalytically" in the subsequent oxidation of these metal ions.

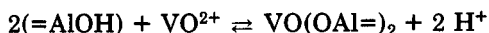
Here we report the results of a comparative study on the oxygenation kinetics of hydrolyzed and adsorbed vanadyl(IV) ion (VO^{2+}). In the case of VO^{2+} , the surface complex formed with Al₂O₃ surfaces has been investigated by ENDOR (electron nuclear double resonance) spectroscopy (Motschi and Rudin).⁹ Thus, the well-characterized nature of the heterogeneous system makes a comparison between the homogeneous and heterogeneous pathways

especially promising. The results obtained confirm that coordinated surface hydroxyl groups produce similar kinetic effects on the oxygenation of VO^{2+} as OH⁻.

In turn, the kinetic results obtained permit us to draw some inferences on the inner-sphere nature of the vanadyl surface complexes formed. In comparing these results to those obtained by others on the oxygenation of Fe(II) and Mn(II), we believe that these findings can be generalized to derive common kinetic factors which control the oxygenation rates of both hydrolyzed and adsorbed metal ions.

The ENDOR experiment by Motschi and Rudin⁹ has been so far the most direct characterization of vanadyl adsorbed to an aqueous oxide suspension. These authors detected a hyperfine coupling of 7.2 MHz between the paramagnetic VO^{2+} and the surface Lewis center ²⁷Al of δ -Al₂O₃. The magnitude of the coupling constant has to be explained by a strong spin delocalization between vanadium and aluminum ions, which implies a short V-Al distance in the range 2.6–3.6 Å.⁹ These results have confirmed the inner-sphere structure of vanadyl at the aqueous oxide interface.

For heterogeneous model systems we use in this study vanadyl adsorbed on δ -Al₂O₃ and on TiO₂ (anatase). In addition to the ENDOR results cited above the thermodynamic and kinetic parameters of the adsorption process are established. Adsorption data are interpreted in terms of the surface complexation model,¹⁰ which involves complex formation equilibria like



where =AlOH denotes a surface hydroxyl group. This procedure allows one to precisely control the oxygenation conditions and to compare the reactivities of the species involved. The homogeneous oxidation of vanadyl by dissolved oxygen has been studied so far only in presence of complex formers¹¹ and in a technical system.¹²

Experimental Section

Materials. δ -Al₂O₃ (Aluminiumoxid C., Degussa) and anatase (Titanoxid P 25, Degussa) with BET areas of 100 ± 15 and 50

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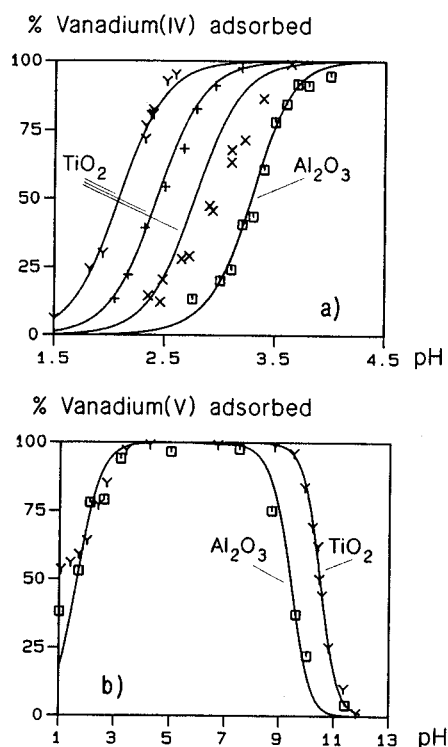


Figure 1. pH dependence of the adsorption of vanadium ions to TiO₂ and δ -Al₂O₃ at $I = 0.1$ and 25 °C, given as percent adsorption relative to total vanadium after 20-h equilibration time. The lines are calculated with the help of the complex formation constants listed in Table I. (a) Adsorption of vanadyl(IV). Experimental conditions from left to right: 10 g/L TiO₂, 2.5×10^{-4} M V(IV)_T; 2 g/L TiO₂, 5×10^{-5} M V(IV)_T; 0.4 g/L TiO₂, 8×10^{-6} M V(IV)_T; 10 g/L Al₂O₃, 2.5×10^{-4} M V(IV)_T. (b) Adsorption of vanadate(V). Conditions: 2 g/L oxide, 5×10^{-5} M V(V)_T.

± 15 m²/g and mean particle sizes of 20 and 30 nm, respectively, were used as aqueous suspensions in double-distilled water. Stock solutions of VO(ClO₄)₂ were prepared from equimolar solutions of VOSO₄ and Ba(ClO₄)₂ and calibrated by titration.¹³

Analysis. Total vanadium was determined by GTA-AAS¹⁴ on a Varian AA 875 spectrometer. Dissolved vanadium(V) was measured selectively even in the presence of a 10-fold excess of vanadium(IV) by using the spectrophotometric method of Budevsky and Johnova.¹⁵ Vanadyl(IV) was analyzed in acid solution at pH 1 by electron spin resonance (ESR)¹⁶ using a Varian E-Line spectrometer operating at the X-band. This technique is very insensitive to large excess of vanadium(V), dissolved aluminum ions, or small amounts of suspended particles.

Adsorption Experiments. Tests of the adsorption kinetics of vanadyl(IV) below pH 4.5 revealed a two-step process: The initial adsorption occurs within a time scale of seconds. The final equilibrium however is attained only within more than 12 h. Therefore, batch experiments were performed to determine the pH dependence of the adsorption equilibria; 50-mL samples containing oxide suspension, vanadium, and 0.1 M NaClO₄ were equilibrated at 25 °C for 20 h. The pH shift due to the dissolution reaction of Al₂O₃ was compensated by an automatic titrator. Total vanadium was determined in the supernatant after centrifugation at 15 000 rpm.

Oxygenation Experiments.¹⁷ All experiments were carried out in a stirred 1-L beaker with a water jacket at constant temperature. The oxygenation kinetics of dissolved aqueous vanadyl was determined in 0.01 M NaClO₄ as a function of pH, [VO²⁺]₀, pO₂, and temperature. Due to the low solubility of VO²⁺ at pH

Table I. Surface Protonation and Complex Formation Equilibria

reaction	constant	δ -Al ₂ O ₃	TiO ₂
exchange capacity, mol kg ⁻¹		0.3	0.46 ^a
Protonation			
=MOH ₂ ⁺ ⇌ =MOH + H ⁺	pK _{a1} ^a	7.4 ^b -10Q	4.5-41Q ^c
=MOH ⇌ =MO ⁻ + H ⁺	pK _{a2} ^a	10-Q	8.0-14Q
Adsorption of V(IV)			
=MOH + VO ²⁺ ⇌ VO(OM=) ⁺ + H ⁺	pK ₁ ^a	0.114	
2(=MOH) + VO ²⁺ ⇌ VO(OM=) ₂ + 2H ⁺	pβ ₂ ^a	1.89	1.34
Adsorption of V(V)			
=MOH + VO ₂ ⁺ ⇌ VO ₂ (OM=) + H ⁺	pK ₃ ^a		-1.48
=MOH + HVO ₄ ²⁻ ⇌ VO ₂ (OH)(OM=) ⁻ + OH ⁻	pK ₄ ^a	1.24	-0.196

^a Value taken from ref 19. ^b Al₂O₃ protonation constants from ref 20. ^c Q stands for the surface charge in mol kg⁻¹.

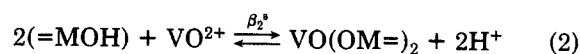
>5, the experiments had to be designed for small concentrations (typically 10 μM). The pH was controlled (a) with the aid of an automatic titrator which contained 0.05 M NaHCO₃ or (b) by using a mixture of O₂/CO₂ at constant alkalinity (HCO₃⁻). Both methods gave equivalent results. The samples taken were stabilized with HClO₄ and analyzed spectrophotometrically for vanadium(V).

The oxygenation kinetics of adsorbed vanadyl was measured in 0.1 M NaClO₄. Vanadyl was adsorbed in the absence of oxygen (N₂-bubbling) slowly by dropping an acid solution of the ion into the oxide suspension at pH 5. After adjustment of the pH, the suspension was allowed to equilibrate for 30 min before the O₂ flow was turned on. No buffer was needed at the typical oxide concentrations of 10 g/L. Some measurements confirmed that more than 99% of total vanadyl remained adsorbed in the initial stage of the reaction. At pH >8 the dissolved vanadium concentration increased slowly during the oxidation experiment to a maximum value of 3% of total vanadium—presumably due to desorption of oxidized vanadates (compare Figure 1b). To stop the reaction, samples were acidified to pH 1 and cooled on ice. The desorption of vanadyl from the oxide phase is rapid ($t_{1/2} \sim 0.3$ h) compared to the oxygenation process ($t_{1/2} \sim 3.5$ h). After complete desorption, the oxide particles were removed by centrifugation and VO²⁺ was analyzed in the supernatant by ESR. All oxygenation experiments were performed at conditions which prevented the formation of polynuclear species, i.e., below the mononuclear wall.

Results

Adsorption. The relevant surface chemical data for anatase and δ -Al₂O₃ were determined by alkalimetric (acidimetric) titration¹⁰ and are shown in Table I. These surface protonation constants were used to evaluate the adsorption equilibria of vanadium ions by the method of Hohl and Stumm.¹⁸

Figure 1a shows the adsorption of vanadyl as a function of pH. The bivalent vanadyl cation is adsorbed at very low pH to the positively charged oxide surface. The adsorption occurs also far below the pH range where hydrolysis becomes dominant. Therefore the following specific equilibria were used to model¹⁸ the adsorption behavior of vanadyl:



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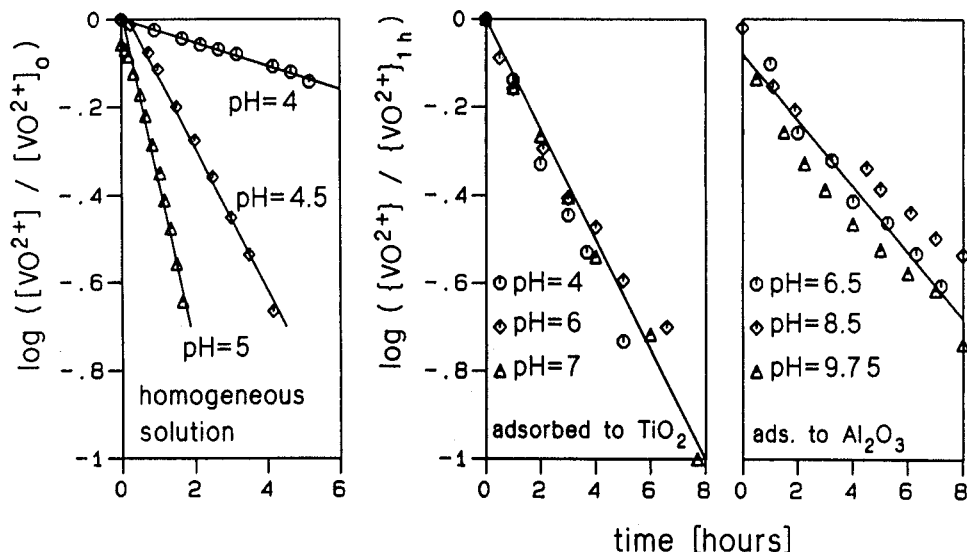
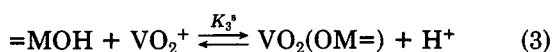
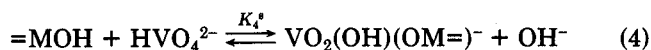


Figure 2. Typical kinetic data of the oxygenation of vanadyl at 25 °C presented as first-order plots. Oxidation rates of adsorbed vanadyl are independent of pH, which is not the case for homogeneous solutions. To minimize experimental artifacts (slow quenching) in heterogeneous systems, parts b and c have been normalized to $\{ \text{vanadyl} \}$ after 1 h.

The adsorption of vanadium(V) (Figure 1b) reflects the complex solution chemistry of these species. At low pH the dioxo cation VO_2^+ is adsorbed specifically despite electrostatic repulsion by a positive surface charge:



A similar strong adsorption of monovalent Np(V)O_2^+ has recently been reported.²¹ At high pH the vanadate ion HVO_4^{2-} reacts like phosphate²² by ligand exchange:



The solid lines in Figure 1 were calculated with the model constants of eq 1–4 and are summarized in Table I. The adsorption curves demonstrate that only trace amounts of vanadyl(IV) will remain dissolved in oxygenation experiments above pH 4, which makes the oxidation of adsorbed VO_2^+ a truly surface-controlled process.

Oxygenation. A comparison of first-order oxygenation plots for vanadyl in homogeneous solution on the one hand, and vanadyl adsorbed to TiO_2 and Al_2O_3 on the other hand, is given in Figure 2. An increase of the oxygenation rate with pH is observed only for dissolved VO_2^+ . In heterogeneous systems a slight deviation from first-order kinetics was found during the first 30–100 min of the experiments. Most probably this apparently faster oxidation of adsorbed VO_2^+ at the outset of the experiments is due to the time required for desorption in the acidified samples. For that reason the oxygenation process could not be quenched by acid as fast as in homogeneous solution. Reaction rates were calculated by using the data for $t > 0.5$ h in the case of TiO_2 and of $t > 2$ h for the Al_2O_3 suspensions. At an excess oxygen concentration ($p_{\text{O}_2} = 1$ atm) an empirical pseudo-first-order rate law

$$-\frac{d[\text{V(IV)}]}{dt} = k_{\text{exp}}[\text{V(IV)}] \quad (5)$$

has been applied, where $[\text{V(IV)}]$ denotes the vanadium(IV) concentration (given in mol m^{-2} in heterogeneous systems and in M for homogeneous solution) and k_{exp} is the first-order rate constant (s^{-1}). The first-order reaction has been

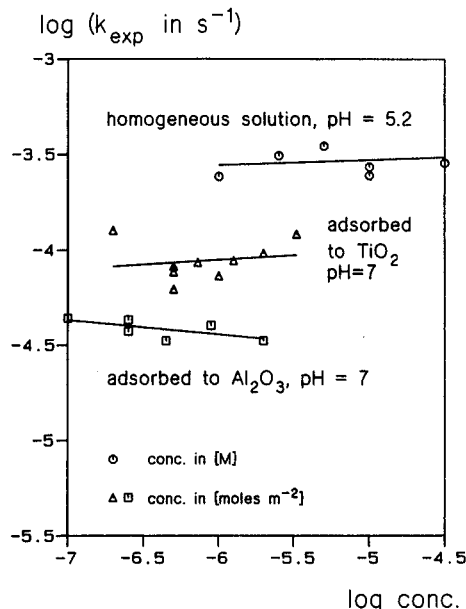


Figure 3. The variation in surface concentration of initial vanadyl has no effect on the empirical rate constant k_{exp} (eq 5), which confirms first-order kinetics in V(IV). Conditions: 25 °C, 1 atm O_2 .

confirmed with a series of experiments where the surface concentration was varied in the range 1–30 μM dissolved and 0.1–3.3 $\mu\text{mol m}^{-2}$ adsorbed VO_2^+ . Figure 3 indicates that the empirical rate constant k_{exp} is independent of the initial concentration of dissolved or adsorbed vanadyl.

Figure 4 collects the results of a series of 38 kinetic experiments with varying pH: although the heterogeneous oxygenation data exhibit some scatter, the dissolution rate is constant over 6 pH units for vanadium(IV) adsorbed to both anatase and $\delta\text{-Al}_2\text{O}_3$. On TiO_2 the oxidation is faster only by a factor of 1.8 compared to Al_2O_3 . The homogeneous oxygenation rate, however, is pH dependent and increases by a factor of 100, raising the pH from 3.5 to 5.5.

A few experiments were performed in order to establish the rate order in molecular oxygen. As Figure 5 shows, the results for homogeneous solutions are compatible with the assumption of oxygen contributing in first order to the rate law. Two additional experiments with heterogeneous systems are in accordance with this finding. In summation

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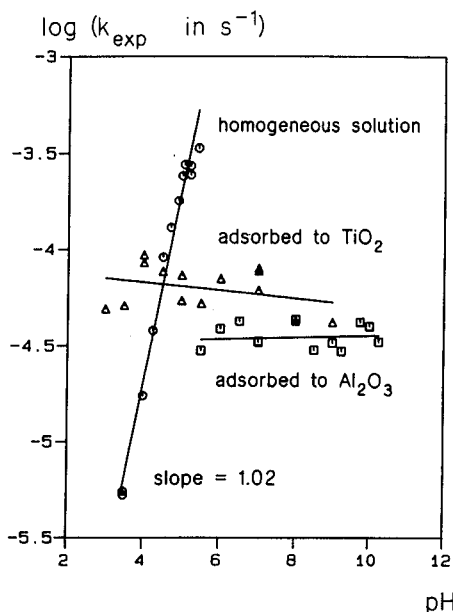


Figure 4. Effect of pH on k_{exp} : the oxygenation rate of aqueous vanadyl increases proportional to $[\text{H}^+]^{-1}$, whereas the reactivity of adsorbed vanadyl is constant over a range of 6 pH units. Conditions: 25 °C, 1 atm O_2 , $[\text{VO}^{2+}]_0 = 1 \times 10^{-6} \text{ M}$, $[\text{V(IV)}]_0$ on $\text{Al}_2\text{O}_3 = 2.5 \times 10^{-7} \text{ mol m}^{-2}$, $[\text{V(IV)}]_0$ on $\text{TiO}_2 = 5 \times 10^{-7} \text{ mol m}^{-2}$.

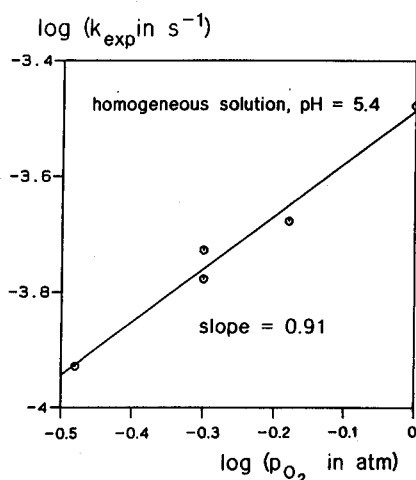


Figure 5. Influence of oxygen partial pressure (atm) on k_{exp} : the experimental slope is compatible with a first-order dependence on $[\text{O}_2]$. Conditions: 25 °C, $[\text{V(IV)}]_0 = 1 \times 10^{-6} \text{ M}$.

of the kinetic results, the empirical rate law for the homogeneous oxygenation of vanadyl can be written as

$$-\frac{d[\text{VO}^{2+}]}{dt} = k_6[\text{H}^+]^{-1}[\text{VO}^{2+}][\text{O}_2] \quad (6)$$

with $k_6 = 1.87 \times 10^{-6} \text{ s}^{-1}$. For the oxygenation of adsorbed vanadyl we deduce the rate law in terms of surface concentrations, $\{\text{V(IV)}\}$ (in mol m^{-2}):

$$-\frac{d\{\text{V(IV)}\}}{dt} = k_7\{\text{V(IV)}\}[\text{O}_2] \quad (7)$$

with $k_7 = 5.13 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for vanadium(IV) adsorbed to TiO_2 and $k_7 = 2.82 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for vanadyl on Al_2O_3 . Thus adsorbed VO^{2+} at 25 °C has independent of pH a half-life of ca. 20 h in air-saturated water.

An Arrhenius plot where the empirical rate constant has been corrected for the temperature dependence of the oxygen solubility is drawn in Figure 6. From the Arrhenius slope apparent activation energies of $E_a = 140 \text{ kJ/mol}$ and 56.5 kJ/mol can be calculated for the homo-

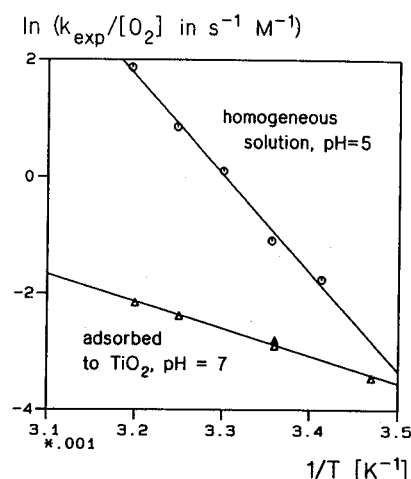


Figure 6. Arrhenius plot. k_{exp} is corrected for the variation in oxygen solubility with temperature. Conditions: 1 atm O_2 , $[\text{V(IV)}]_0 = 1 \times 10^{-6} \text{ M}$, $[\text{V(IV)}]_0$ on $\text{TiO}_2 = 5 \times 10^{-7} \text{ mol m}^{-2}$.

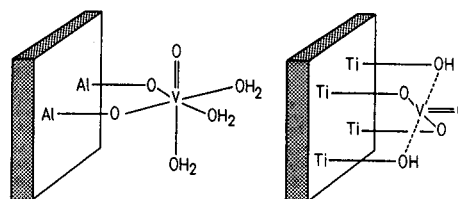


Figure 7. Postulated structures of adsorbed vanadyl (in analogy to Motschi²⁴).

geneous oxygenation at pH 5 and the oxidation of vanadyl adsorbed to TiO_2 at pH 7, respectively.

Discussion

Adsorption. The observations (i) that vanadyl adsorbs at low pH against a strong positive surface charge and (ii) that the adsorption occurs far below the pH range of hydrolysis both support an inner-sphere coordination of VO^{2+} to surface OH groups. Kinetic studies (pressure jump technique) on adsorption and desorption of other metal ions on $\delta\text{-Al}_2\text{O}_3$ clearly support the surface complex formation model.²³ Two probable coordination geometries are shown in Figure 7. Inner-sphere coordination of adsorbed VO^{2+} has been deduced from different ESR studies²⁵ and has been confirmed by ENDOR.⁹ The pH dependence of the adsorption equilibria gives some evidence that two surface OH groups are coordinated at pH > 4.5. Therefore, we use in the following discussion the notation $\text{VO}(\text{OM})_2$ for surface-bound V(IV).

Rate Law. The rate laws given for the oxygenation of V(IV) in homogeneous solution can be interpreted in terms of a rate dependence in hydroxovanadyl, $\text{VO}(\text{OH})^+$

$$-\frac{d\{\text{V(IV)}\}}{dt} = k_8[\text{VO}(\text{OH})^+][\text{O}_2] \quad (8)$$

and may be compared with that of the surface-controlled reactions of V(IV) bound to hydrous Al_2O_3 or TiO_2

$$-\frac{d\{\text{V(IV)}\}}{dt} = k_9\{\text{VO}(\text{OAl})_2\}[\text{O}_2] \quad (9)$$

$$-\frac{d\{\text{V(IV)}\}}{dt} = k_{10}\{\text{VO}(\text{OTi})_2\}[\text{O}_2] \quad (10)$$

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Table II. Kinetics of Oxygenation of V(IV), Fe(II), and Mn(II)

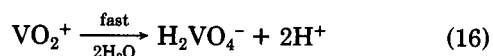
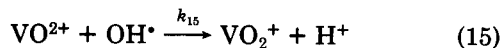
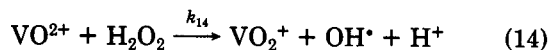
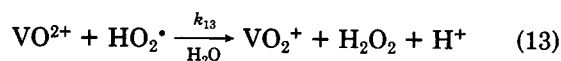
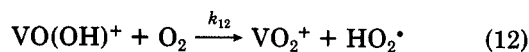
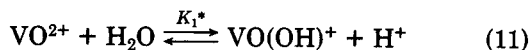
species	solid phase	k , $M^{-1} s^{-1}$	ref
VO^{2+}		$<1 \times 10^{-6}$ ^a	this work
$VO(OH)^+$		1.07	this work
$VO(OAl=)_2$	δ - Al_2O_3	0.028	this work
$VO(OTi=)_2$	anatase	0.051	this work
Fe^{2+}		7.7×10^{-4} ^b	29
$Fe(OH)^+$		22.5	30 ^c
$Fe(OH)_2$		5.7×10^6	30
$Fe(OFe=)_2$	am FeOOH	~ 35	7 ^d
$Fe(OFe=)_2$	β -FeOOH	~ 5	7
$Mn(OH)^+$		$<5 \times 10^{-4}$	31 ^e
$Mn(OH)_2$		<0.6	31
$Mn(OFe=)_2$	γ -FeOOH	0.69	8
$Mn(OAl=)_2$	δ - Al_2O_3	<0.07	8

^a Estimated with the help of data by Post and Robins.¹²

^b Constant is second order in Fe(II) ($M^{-2} s^{-1}$). ^c Data interpretation based on results by Stumm and Lee.² ^d Data represent order of magnitude because surface area concentrations were not determined. ^e Based on observations according to which Mn(II)_{aq} at pH 8.3 persists for a half-life of more than 10 years.

Comparison of eq 8–10 shows that the surface-bound vanadyl acts with oxygen in a similar way as a reactant with the deprotonated vanadyl.

The reaction mechanism that could account for the rate law of eq 8 can be derived from the Haber–Weiss scheme:²⁶



The rate-determining step is believed to be eq 12. The subsequent one-electron steps are fast²⁷ and have no influence on the first-order dependence with respect to O_2 and $VO(OH)^+$. Thus, $[VO(OH)^+]$ in eq 8 and 12 can be replaced by $K_1^*([H^+] + K_1^*)^{-1}[V(IV)]$. This rate law is compatible with the data obtained by Post and Robins¹² under technical conditions (70–150 °C) in acid solutions (pH 0.5–2.5); thus, it may be inferred that eq 8 holds within the pH range 0.5–5.5.

The kinetic constants determined are compared in Table II. Obviously, complex formation with hydroxide in solution or with hydroxide surfaces enhances the reactivity of vanadyl toward oxidation by molecular oxygen by more than 3 orders of magnitude. The similarity of the magnitude of these rate constants is remarkable; the constant for the hydrolyzed V(IV) species is within a factor of 20 and 35, respectively, of that for the vanadyl adsorbed to hydrous TiO_2 and to Al_2O_3 . That the reactivity of soluble hydroxo complexes is somewhat higher than that of complexes with surface oxygen donor groups is to be expected: the functional groups are bound into a solid framework; their reactivity is, in essence, a cooperative property (Sposito).²⁸ Surface OH groups are also more acidic and

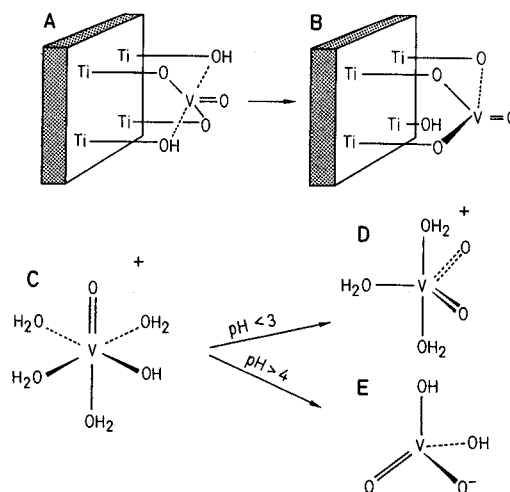


Figure 8. Structural changes during oxidation of V(IV) require different activation energies: only a small change in coordination would be necessary on oxidation of the postulated adsorbed V(IV) species A. The oxidation of dissolved $VO(OH)^+$ (C) requires more activation energy at low pH (product D) than at pH > 4, where tetrahedral vanadate (E) is formed.

weaker σ -donors than free OH^- .

Inner-Sphere Nature of Vanadyl Surface Complexes. The acceleration of the oxygenation of vanadyl by adsorption to hydrous oxides and the similarity of the rate constants measured for soluble hydroxo and for surface complexes represent strong corroboration—in addition to the spectroscopic (ESR and ENDOR) evidence procured by Motschi and Rudin⁹—that the vanadyl adsorbed to these oxides represents an inner-sphere type of surface complexes. It seems highly unlikely that VO^{2+} adsorbed in an outer-sphere complex (i.e., in the outer Helmholtz plane) would be oxidized by oxygen more than 1000 times faster than the dissolved VO^{2+} (see Table II). It is thus justified to treat these surface species in rate laws as kinetic entities.

Activation Energy. An explanation is needed to account for the differences in activation energies between homogeneous and heterogeneous reactants. One first needs to consider that, in the case of the homogeneous reaction, the activation energy includes the temperature dependence of the hydrolysis reaction ($\Delta H^\circ = 54.4 \text{ kJ mol}^{-1}$)³² that precedes the rate-determining reaction. In the heterogeneous systems the surface complexes $VO(OM=)_2$ are the dominant species in the pH range of our experiments. Their concentrations are therefore insensitive to changes in temperature. Second, the difference of about 30 kJ mol^{-1} that still remains between homogeneous and heterogeneous reactions may perhaps be accounted for by assuming that, in the case of soluble $VO(OH)^+$, part of the energy needed is used for the transition from an octahedral symmetry to a tetrahedral one (Figure 8). Post and Robins¹² observed an activation energy of 96.5 kJ/mol for the oxygenation of dissolved vanadyl at pH < 2.5, which has to be compared with our value of 140 kJ/mol at pH 5. The difference in activation energy between high and low pH may be explained by inferring that the extent of symmetry change is smaller in acid solution than at pH 5. At the surface, however, it may suffice to deprotonate a bridged OH group and to loosen the bond to another

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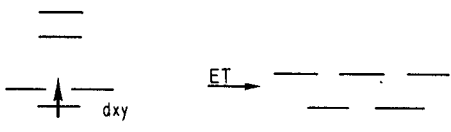
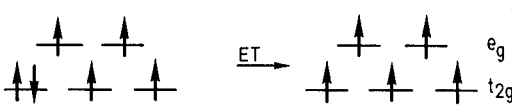
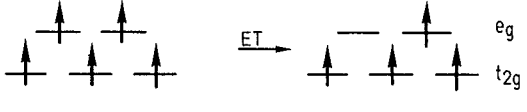
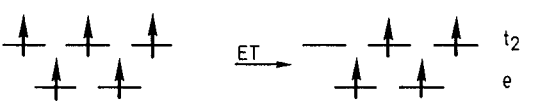
Observed oxygenation rate	Coordination shell	Change in electronic structure
$V(IV)_{aq.} \xrightarrow{\text{fast}} V(V)_{aq.}$	distorted octahedron	
$Fe(II)_{aq.} \xrightarrow{\text{fast}} Fe(III)_{aq.}$	octahedron	
$Mn(II)_{aq.} \xrightarrow{\text{slow}} Mn(III)_{aq.}$	octahedron	
$Mn(II)_{ads.} \xrightarrow{\text{fast}} Mn(III)_{ads.}$	(hypothetical) tetrahedron	

Figure 9. Relation between electronic structure and oxygenation kinetics. Apparently the transfer of an electron from a d_{xy} , d_{xz} , or d_{yz} orbital of V(IV) or Fe(II) to O_2 occurs much faster than the transfer from an orbital with e_g symmetry ($d_{x^2-y^2}$, d_{z^2}), as in the case of Mn(II). One may assign the fast oxygenation of adsorbed Mn(II) to a difference in coordinative structure.

=TiOH group in order to form an uncharged vanadate surface species.

Comparison with Fe(II) and Mn(II). The acceleration of oxygenation rates by hydrolysis has been observed for many other metal ions; an equivalent rate law has been observed for Ti^{3+} ,³ V^{3+} ,⁴ and $U(IV)$.⁵ In the case of Fe^{2+} ,^{2,7,30} the enhancement of the oxidation rate by hydroxo complex formation is paralleled by that of complex formation with oxygen donor groups of oxide surfaces (Table II). Deprotonation of the aquo Fe(II) ion enhances the autooxidation by more than 10^4 ; $Fe(OH)_2$ reacts 10^5 times faster than $Fe(OH)^+$. Hydrolysis of VO^{2+} promotes the oxygenation kinetics by the same order of magnitude as that observed for Fe^{2+} . The adsorbed surface complexes of both metal ions react with similar rate constants as the corresponding monohydroxo complex in solution.

$Mn(II)$ ^{8,31} behaves somewhat differently than Fe(II) and V(IV); dissolved $Mn(OH)^+$ is slower by a factor of more than 10^3 than the surface-bound Mn(II). Obviously, surfaces provide a special activation for Mn(II).

It is well-known³³ that electronic structure is an important factor influencing the redox kinetics. For example, in the case of the oxidation of Mn(II), one electron needs to be removed from the e_g orbital (d_{z^2} , $d_{x^2-y^2}$), whereas in the oxidation of VO^{2+} , the sole electron lies in the d_{xy} orbital (Figure 9). It appears that the coordination arrangement offered to the Mn^{2+} ion in surface complex permits an oxidation by O_2 that is characterized by a much smaller activation energy than that in the oxygenation of $Mn^{2+}(aq)$. Plausibly, Mn(II) may be coordinated tetra-

hedrally or quadratically. Because of the changed ligand field splitting, the oxidation results from the removal of an electron from the higher t_2 orbital (Figure 9); i.e., the removal of the electron has less consequence on the coordination shell, and the formation of an activated complex needs less energy.

Conclusions

The rate of oxidation of V(IV) by oxygen in aqueous media is significantly enhanced by hydrolysis or adsorption to hydrous oxide surfaces; it is proportional to the concentration of hydroxovanadyl in solution or to that of the surface complexes of vanadyl with hydroxo groups present on the surface of hydrous Al_2O_3 or TiO_2 . The formal congruence of the rate laws for the homogeneous and heterogeneous systems and the similar magnitude of the respective rate constants substantiate the inner-sphere nature of the vanadyl surface complexes in support of the earlier characterization by ENDOR spectroscopy.⁹ A comparison with published data on the autooxidation of dissolved and surface-bound Fe(II) and Mn(II) leads to the generalization that the reactivity of transition-metal ions toward oxidation by oxygen is strongly influenced by (i) the coordination of oxygen-donor ligands like dissolved OH^- and surface bound $=MO^-$ and (ii) the electronic structure of the reactant complex.

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Registry No. VO^{2+} , 20644-97-7; VO_2^+ , 18252-79-4; Al_2O_3 , 1344-28-1; TiO_2 , 13463-67-7.

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