When thiocyanate ion is in the coordination sphere of $VO^{2+}(aq)$ in acidic media, the rate constant for exchange decreases. The rate constant ratio for H_2O to NCS^- is about 40 ± 20. Most of the error is in the k_0 term for H_2O. An effect of this magnitude could be caused by (1) electron withdrawal by π bonding of NCS^- in the axial position or (2) equatorial coordination and the loss of an equatorial water site for exchange. From the studies on the multidentate ligands both (1) and (2) are probably responsible for the effect seen.

To test the possibility of involvement of equatorial water in the predominate exchange mechanism, three multidentate ligand complexes ($C_2O_4^{2-}$, NTA^{3-}, and $EDTA^{4-}$) were studied. Their solution structures are reasonably well established by NMR.[9] The oxalate complex is trans and thus has only axial water, the NTA^{3-} complex may have equatorial water,[16] and the $EDTA^{4-}$ complex ion has no coordinated water. In all the complex ions, the charge is negative, which should increase the rate constant, and in the more acidic regions, there is a tendency to protonate and partially dissociate the ligand. With the oxalate or $EDTA^{4-}$ complexes the exchange rate essentially stopped in the neutral region and was faster than the parent ion, $VO^{2+}(aq)$, at a pH of 1.5. This strongly suggests that an equatorial water is necessary for exchange to occur and is provided in the acidic range by partial dissociation of the organic ligand facilitated by protonation. The negative charge on the complexes and the presence of the chelate ligands in the other equatorial positions would be expected to cause the yl-oxygen exchange to be faster than in the parent ion. For the NTA^{3-} complex, which is the only complex thought to possess an equatorial water, the pH behavior is entirely different. The observed rate of exchange is rapid at a pH of 3 and becomes too large to measure at a pH of 6.5.

While the aqueous structure of the NTA^{3-} complex is not certain and solutions may contain appreciable equilibrium amounts of other species having the water in an axial position or even a pyramidal form, it is clear that, with this ligand, complexes containing equatorial water would be much more available than the $EDTA^{4-}$ or oxalate complexes. Thus, we suggest that the equatorial water is intimately involved in the mechanism of the yl-water exchange and that, in the more alkaline region, deprotonation of the coordinated water results in a hydroxy species, present in only small amounts, which carries the exchange in the same manner postulated for the OH^- term of the aquo ion.

The activation parameters for $VO^{2+}(aq)$–H_2O exchange of $\Delta H^{\ddagger} = 20.5 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = -4.4 \pm 0.2$ cal/(mol deg) are for a composite of the aquo and the hydroxo terms. At the acidity used (0.1 M), it is estimated that they reflect 85% of the k_0 term and 15% of the k_{OH} term. The high activation enthalpy and the small negative entropy changes in going to the activated complex are not out of line with the proposed intramolecular electronic rearrangement (IER) mechanism proposed.

In conclusion, we suggest that the IER mechanism may be a general feature of many yl-oxygen solvent exchange processes and it requires that a cis-aquo, -hydroxo, or -oxo group be present or generated to provide this lower energy path for exchange.

Acknowledgment. We thank the Research Council, University of Missouri, for support of certain phases of the work.

Registry No. H_2O, 7732-18-5; $VO(OH_2)_4^{2+}$, 36737-80-1; $VO_2(OH_2)_4^+$, 81738-79-6; $CsNH_4[VO(C_2O_4)_2OH_2]\cdot H_2O$, 84710-12-3; $((CH_3)_4N)_3[VO(NCS)_5]$, 22608-76-0; $[VO(NTA)OH_2]^-$, 12347-63-6; $[VO(EDTA)]^{2-}$, 20648-98-0; HCl, 7647-01-0; oxygen, 7782-44-7.

---

(16) Nishizawa, M.; Saito, K. *Inorg. Chem.* **1978**, *17*, 3676. The crystal structure of a VO^{2+} complex with a similar ligand, ((2-pyridylmethyl)imino)diacetate, has only equatorial (basal) water and appears to retain this structure in solution even on substitution.

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201

Isotopic Oxygen Exchange between $VO_2^+(aq)$ and Solvent Water

K. M. RAHMOELLER and R. KENT MURMANN*

Received May 11, 1982

The ^{18}O isotopic oxygen exchange of the oxo (yl) oxygens of *cis*-$VO_2^+(aq)$ is too rapid to measure by static methods. Studies using the rapid formation of $[VO_2(C_2O_4)_2]^{3-}$, followed by $[Co(en)_3]^{3+}$ precipitation, revealed complete oxygen exchange during the conversions. Studies on the yl-oxygen exchange of *cis*-$[VO_2(C_2O_4)_2]^{3-}$ found the rate to be less and the rate equation to be rate = $k_0[VO_2(C_2O_4)_2]^{3-} + k_h[H^+][VO_2(C_2O_4)_2]^{3-}$, where $k_0 = 0.31 \pm 0.1$ s^{-1} and $k_h = (4.7 \pm 1) \times 10^3$ s^{-1} M^{-1} at 0 °C and a pH <6. Above this pH a chemical modification occurs and the observed rate increases with pH. An impurity, presumably V(IV), also increases the rate. It can be removed with traces of $H_4IO_6^-$, which oxidizes it to V(V). $VO_2^+(aq)$ is rapidly reduced and complexed by excess NCS^- to $VO(NCS)_5^{3-}$, which exchanges its yl oxygen slowly. Competition between ^{18}O-solvent exchange and NCS^- reduction allows an estimation of the intrinsic exchange rate of $VO_2^+(aq)$. At 0 °C the $t_{1/2}$ of 0.15 s was estimated ($k = 4.7$ s^{-1}).

Introduction

Metal ions of high oxidation state often exhibit unusual structural properties in aqueous media. Governing the structural behavior are two main forces: the formation of multiply bonded oxygen atoms (yl type) and polymerization through oxy or hydroxy bridges. The kinetic nature of the metal–oxygen bonds in these aqueous metal ions is of fundamental importance in understanding and predicting their behavior in a host of situations and conditions.

The formulation of vanadium(V) as VO_2^+ in acidic media was made early in the history of chemistry primarily on the basis of the formula of complexes crystallized from acidic water solutions. Only recently, however, has it been shown that there is a high degree of certainty that the cis configuration is preferred.[1,2] This conclusion comes from IR, NMR, and X-ray crystal structure studies. Few, if any, other examples of *cis*-dioxoaquo ions have been established with the same degree of assurance. Molecular orbital predictions are

---

(1) Scheidt, W. R.; Tsai, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867.

(2) Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3873.

in agreement with the experimental conclusions with regard to the cis structure.[3]

A considerable body of evidence has been accumulating on the question of the rate of oxy, hydroxo, and aquo group exchange *within an ion*, internal rearrangement (IER). Such a process requires only proton transfer (which ought to be rapid), electron rearrangement within an ion (which probably is fast), and a reorganization of metal–oxygen distances (which may be highly variable) in rate. For the systems for which there are firm data, on yl to OH or OH_2, the internal rearrangement (IER) process is found to be slow.[4] However VO_2^+(aq) is the first test of an ion in which a cis-oxo configuration is known. While it is not possible at the present time to determine whether the oxo oxygen exchanges with the solvent water or whether it interchanges with a water molecule in the first coordination sphere (which then exchanges rapidly with the solvent), this work and that on VO^{2+} suggest that the IER model mechanism can be important and should be considered.

Thus this paper describes work the aim of which is to determine the rate constant of water exchange with the yl oxygens of VO_2^+ and to compare it with that of $[VO_2(C_2O_4)_2]^{3-}$, where equatorial waters are not available to enter into an ir mechanism.

Experimental Section

$Na_6V_{10}O_{28}\cdot 8H_2O$ was prepared from recrystallized $Na_3VO_4\cdot nH_2O$ by the method previously described.[5] After recrystallization it was used to prepare solutions of $VO_2^+(aq)ClO_4^-$ (as concentrated as possible) by using a modification of the technique developed by Johnson.[6] A 3.5-g sample of $Na_6V_{10}O_{28}\cdot 18H_2O$ in 75 mL of water was passed through a Dowex 50W-X8 H^+ resin (2.5-fold excess capacity). The column was rinsed rapidly with 50 mL of water, and the combined eluent was treated with 15.2 mL of 11.8 M $HClO_4$. This solution was diluted to the required concentration. In practice, stable solutions of $[VO_2^+] \sim 0.2$ M were obtained in 1.0 M $HClO_4$. When the presence of ClO_4^- was objectionable, CH_3SO_3H was interchanged without other modifications. Standardization for VO_2^+ was by titration with Fe(II) using the method of Walden, Hammett, and Edmonds.[7]

$(NH_4)_3[cis\text{-}[VO_2(C_2O_4)_2]\cdot 2H_2O$ was prepared by the method of Sathyanarayana and Patel[8] without H_2O_2 but was always contaminated by a slightly soluble white impurity. Slow evaporation of concentrated solutions produced large (1 cm^2) clear yellow crystals, which were physically removed and again recrystallized. These crystals were extremely stable in clean air but decomposed in the presence of acidic fumes. Once formed and freed of excess oxalate ion, a solution of the complex could be boiled without perceptible internal oxidation–reduction. Anal. Calcd for $(NH_4)_3VO_2(C_2O_4)_2\cdot 2H_2O$ $(VO_{12}N_3C_4H_{14})$: V_2O_5, 26.1; C, 13.76; N, 12.04; H, 4.62. Found: V_2O_5, 26.2; C, 13.76; N, 11.92; H, 4.64.

$(NH_3)_4[cis\text{-}VO_2(EDTA)]$ was prepared by using an adaptation of the method of Przyborowski.[9] Recrystallization to large single crystals was again used for purification. Anal. Calcd for $(NH_3)_4[VO_2(EDTA)]$ $(VO_{10}C_{10}N_5H_{24})$: C, 28.24; N, 16.47; H, 5.69. Found: C, 28.19; N, 16.46; H, 5.72.

$Cs(NH_4)[VO(C_2O_4)_2]$ was supplied by Johnson.[4] All other compounds were of reagent grade. The water was distilled and deionized with a double-bed resin. The ^{18}O water was normalized with respect to deuterium and distilled from alkaline $KMnO_4$ solution.

Isotopic analysis was made on CO_2 prepared by decomposition of the oxygen-containing compounds in the presence of HgI_2 at 375 °C for $^1/_2$ h in break-seal tubes. Impurities were removed by separation by GPC on a silicone oil–firebrick column. A Nuclide RMS-16 mass spectrometer was used to measure the 46/(44 + 45) ratio, which was normalized to a standard CO_2 sample that was arbitrarily given a value of 4.00×10^{-3}. For water samples, equilibration with a small amount of CO_2 was employed (3 days at 25 °C), followed by separation and measurement of the ^{18}O content of CO_2 with suitable corrections for isotope fractionation.[10]

VO_2^+–OH_2 Exchange (Oxalate Method). The primary purpose of this investigation was to determine the number of "slowly exchanging" oxygens in the ion of V(V) in acidic media and to investigate their rate of exchange with solvent. To accomplish this, a relatively rapid change in the isotopic composition of the solvent of a V(V) solution was made, followed by precipitation of a well-defined solid containing the ion. After extensive exploratory studies no suitable precipitant was found. Only hexacyanometal complexes brought the ion out, but the solids were not suitable for isotopic analysis. Another method often employed, sampling the water, is not applicable here because of the low maximum concentration of V(V), the small number of oxygens, and the rapid reaction rate (vide infra).

Complexation of V(V) with oxalate ion is rapid, and the ion, *cis*-$[VO_2(C_2O_4)_2]^{3-}$, is rapidly and completely precipitated with $[Co(en)_3]^{3+}$. Anal. Calcd for $[Co(en)_3][VO_2(C_2O_4)_2]$ $(VCoO_{10}N_6C_{10}H_{24})$: Co 11.8; N, 16.87; C, 24.11; H, 4.86. Found: Co, 12.0; C, 23.93; N, 16.66; H, 4.97.

A 0.50-mL sample of ^{18}O-enriched water was mixed with 0.50 mL of a $Na_2C_2O_4$ solution (2.86 g/100 mL) and 0.025 mL of a saturated solution of $[Co(en)_3]Cl_3$ added. After the mixture cooled to 0 °C, 0.15 mL of a 0 °C, 0.10 M VO_2^+ solution was injected with vigorous magnetic stirring. Precipitation was immediate. The solid was immediately centrifuged, washed twice with methanol and twice with anhydrous ether, and then dried under vacuum (10^{-5} mm) overnight. The ^{18}O content of all oxygens in the yellow precipitate was determined by conversion to CO_2. Under the conditions of the experiment, no solvent oxygen exchange with oxalate ion occurs.[11]

VO_2^+–H_2O Exchange (Thiocyanate Method). Since the rate of yl-oxygen exchange appeared to be very fast, a competitive method for estimating the rate seemed appropriate. Since it was previously shown[4] that VO^{2+} is slow to exchange and that $VO(SCN)_5^{3-}$ is easily analyzed for its ^{18}O content, it appeared that a fast reduction to VO^{2+} might be competitive with (and effectively stop) oxygen exchange. A rapid reductant is NCS^-, which can also be used as the complexinng agent.

A saturated solution (0.4 mL) of KNCS in $H_2{}^{18}O$ was cooled to 0 °C and injected into 1.5 mL of a rapidly stirred 0.16 M VO_2^+–HSO_3CH_3 solution. Instantly a deep blue color (V(IV)) developed. The solution was added to 1.0 mL of a saturated KNCS–$(CH_3)_4NBr$ solution. A blue precipitate formed immediately, $((CH_3)_4N)_3[VO(NCS)_5]$. The latter was separated by centrifugation, washed twice with cold 1-propanol and twice with anhydrous ether, and vacuum dried (10^{-5} mm) overnight. The solid was baked at 375 °C for $^1/_2$ h with HgI_2 in a sealed tube, and CO_2 was collected, purified, and analyzed for ^{18}O. For the "∞-time" samples, NCS^- was added after VO_2^+ had ample time for exchange and the other operations remained the same.

***cis*-$[VO_2(C_2O_4)_2]^{3-}$–H_2O Exchange.** Exactly 0.15 ± 0.01 mL of a $[VO_2(C_2O_4)_2]^{3-}$ solution at the appropriate concentration was injected via a pressure pipet into 1.05 ± 0.01 mL of $H_2{}^{18}O$ which contained about 2× ^{18}O enrichment. A close-fitting magnetic stirring bar in a 2.0-mL flat-bottomed flask was cooled in an ice bath, and the injected liquids were also maintained at 0 °C. After a measured interval following the first injection, 0.025 mL of a saturated $[Co(en)_3]Cl_3$ solution was injected to cause precipitation of a yellow-orange product, which was analyzed to be $[Co(en)_3][VO_2(C_2O_4)_2]$. It was collected by centrifugation, washed twice with methanol and twice with ether, and then dried overnight under vacuum. Isotopic oxygen analysis was as previously described.

Because of the rapidity of the reaction, $t_{1/2} \sim 2$ s, each point was taken separately and the time of contact measured electronically as determined by contacts on the syringes. Experiments demonstrated

---

(3) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, *400*.

(4) Murmann, R. K. *Inorg. Chim. Acta* **1977**, *25*, 43. Johnson, M. M.S. Thesis, University of Missouri, 1981 (*Inorg. Chem.*, preceding paper in this issue).

(5) Shriver, D. F. *Inorg. Synth.* **1979**, *19*, 140.

(6) Johnson, G. K. Ph.D. Thesis, University of Missouri, Columbia, MO, 1977.

(7) Walden, G. H.; Hammett, L. P.; Edmonds, S. M. *J. Am. Chem. Soc.* **1934**, *56*, 57.

(8) Sathyanarayana, D. N.; Patel, C. C. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1736.

(9) Przyborowski, L.; Schwarzenbach, G.; Zimmermann, Th. *Helv. Chim. Acta* **1965**, *48*, 1556.

(10) Hunt, J. P.; Taube, H. *J. Chem. Phys.* **1951**, *19*, 602.

(11) Bunton, C. A.; Carter, J. H.; Llewellyn, D. R.; O'Connor, C.; Odell, A. L.; Yih, S. Y. *J. Chem. Soc.* **1964**, 4615.

that the rate of stirring had no effect on k_{obsd} above a minimum value, that the time error was about ±0.05 s, and that there was about 8% induced exchange that could not be prevented. Most of this exchange was shown to be with the solid during washing, and so the time of the centrifugation steps was kept small and was the same for all samples.

It was obvious from the infinity-time value and the linearity of $-\ln(1-F)$ vs. time plots that only 2 of the 10 oxygens in the solid complex ion were exchanging (the yl oxygens). To establish that no oxalate ion oxygen exchange occurred, the complex was made to dissociate during an exchange run and oxalate ion precipitated with Pb^{2+}. The $Pb(C_2O_4)$ obtained contained no enrichment (±1%), even after 6 half-times for yl-oxygen exchange.

Initial experiments demonstrated a slight nonreproducibility of the rate, which was removed by oxidizing agents and led to a rate decrease. The catalysis is attributed to the traces of $VO^{2+}(aq)$ in the original complex. Since oxalate ion is a good reducing agent for V(V), it is not surprising that traces of V(IV) are present. The presence of $Cr_2O_7^{2-}$ or $H_4IO_6^-$ (0.2–1.0 h) removes this problem by giving identical first-order exchange graphs. In the presence of $H_4IO_6^-$ different preparations of the complex ion gave the same k_{obsd}.

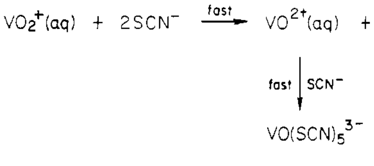
$[VO_2(EDTA)]^{3-}$–H_2O Exchange. A 0.15-mL sample of a 0.16 M $[VO_2(EDTA)]^{3-}$ solution was injected into 1.05 mL of a solution containing $H_2{}^{18}O$. At intervals, 0.3 mL of a UO_2^{2+} solution was added and the precipitate $[UO_2]_3[VO_2(EDTA)_2]\cdot nH_2O$ was collected, washed with methanol and then with ether, and then dried under vacuum. In one run the UO_2^{2+} was equilibrated with ^{18}O water before its addition to the vanadium complex solution. The reactions were conducted at 0 °C at a pH of 7.0 without the addition of $H_4IO_6^-$.

VO_2^+–NCS^-—Rates of Reduction. The rate of reduction of VO_2^+ with NCS^- producing VO^{2+} was studied in acid solutions by using stopped-flow techniques. The disappearance of VO_2^+ at 440 nm was measured under conditions similar to those for the ^{18}O-transfer experiments. Because of the large $[NCS^-]$ excess, pseudo-first-order kinetics were observed. The data were analyzed with use of an exponential least-squares curve-fitting program. The experimental error was high due to the differences in viscosity of the salt solutions being mixed, which were required in order to be similar to the conditions of the VO_2^+–H_2O exchange studies.

Results

a. Preliminary Results on VO_2^+–OH_2 Exchange. Four attempts were made to precipitate VO_2^+ as $[Co(en)_3][VO_2(C_2O_4)_2]$. At 0 °C with $[VO_2^+] = 0.10$ M in 0.50 M $HClO_4$ the amount of oxygen exchange completed on the isolated solid was 98.6, 104.3, 102.8, 100.7% (average 101.6 (2.5)%). Since the solid formation occurred "instantaneously", either the exchange rate of the yl oxygens with solvents is extremely rapid ($t_{1/2} < 0.1$ s) or total exchange was caused by the complexation and precipitation process. At this point it is not possible to distinguish between these possibilities.

b. VO_2^+–H_2O Exchange Rate by SCN^- Competition. The reduction of VO_2^+ with SCN^- to VO^{2+} is very rapid (eq 1),



$$\begin{tikzcd} VO_2^+(aq) + 2SCN^- \arrow[r, "fast"] & VO^{2+}(aq) + (SCN)_2 \arrow[d, "fast"', "SCN^-"] \\ & VO(SCN)_5^{3-} \end{tikzcd} \qquad (1)$$

and it is known that VO^{2+} exchanges its yl oxygen with solvent very slowly ($t_{1/2} \sim 300$ min at 0 °C).[4] Furthermore, there is ample evidence from other systems that oxygen retention can occur upon reduction. In the presence of excess SCN^- the complex ion $VO(SCN)_5^{3-}$ is very rapidly formed and can be crystallized from solution as anhydrous $[(CH_3)_4N]_3[VO(SCN)_5]$, whose oxygen isotope ratio can be easily determined. Thus, VO_2^+ added to ^{18}O-enriched water containing a large excess of SCN^- can exchange oxygens only if the VO_2^+–H_2O exchange rate is comparable to or faster than its reaction with SCN^-. The isotopic composition of $VO(SCN)_5^{3-}$ will reflect the relative rates of exchange/reduction *if* a VO_2^+ oxygen is retained during reduction. The results given in Table I show (a) that competition is present and repeatable and (b) that oxygen atom retention does occur upon reduction. The percent completion of exchange was calculated from the initial value of VO_2^+ (from the water), the final value when SCN^- was added after oxygen exchange was complete, and the ^{18}O content of $[(CH_3)_4N]_3[VO(NCS)_5]$ obtained with competition. Increasing the acidity caused the exchange/reduction ratio to decrease, whereas having $H_4IO_6^-$ present in the VO_2^+ stock solution had no effect. Since either the ^{18}O exchange rate or the SCN^- reduction may be affected by these solution environment changes, no conclusions can be drawn as to the effects of these changes on the individual rate constants.

Table I. VO_2^+–$H_2{}^{18}O$ Exchange Results (SCN^- Competition)[a] ($[SCN^-] = 5.0$ M)

run	% completion of exchange[b]	run	% completion of exchange[b]	run	% completion of exchange[b]
1	94.2	5[c]	81.7	9[d]	55.4
2	83.6	6[c]	77.9	10[d]	64.9
3	80.2	7[c]	77.3	11[e]	57.5
4	86.1	8[c]	78.3	12[e]	57.2

[a] At 0 °C; $[VO_2^+] = 0.126$ M; $[CH_3SO_3H] = 1.0$ M. [b] Based on the measured zero and infinity values. [c] Small amount of $NaIO_4$ present. [d] $[CH_3SO_3H] = 1.5$ M. [e] $[CH_3SO_3H] = 2.0$ M.

Table II. Rate of $VO_2^+(aq)$ Reduction by SCN^-

$[H^+]$, M	k_{obsd}, s^{-1}	conditions
0.005	20.7 (1.0)	$[VO_2^+] = 0.0016$ M
0.05	20.8 (1.4)	$[SCN^-] = 5.0$ M
0.50	32.2 (7)	0.0 °C
1.00	38.9 (1.3)	

In order to estimate the magnitude of the exchange constant and to discern what is affected by the addition of H^+, the rate of the VO_2^+–SCN^- reduction reaction was studied by stopped-flow methods independent of exchange but under comparable conditions. While the accuracy is poor, due presumably to the high rates and the viscosity and density differences between the two mixing solutions, the rate appears to be $[H^+]$ sensitive. The rates of reduction studies appear in Table II.

Since the rate of VO_2^+ reduction by SCN^- has a positive hydrogen ion dependence, the decreased exchange with increasing acidity noted in Table I can be accounted for without introducing an acid dependency into the rate equation for oxygen exchange. A more quantitative evaluation is not possible with present data due to its inherent imprecision.

It is possible, however, to estimate the rate constant for VO_2^+–H_2O exchange assuming (a) 86% exchange (average), in the competition experiments, (b) second-order reduction of VO_2^+ to VO^{2+}, (c) oxygen retention to be complete in the reduction, (d) that oxygen exchange competes with SCN^- reduction but does not compete for a common intermediate. For all but (c) and (d) there is some previous justification, and the latter two are reasonable. Utilizing these assumptions and the standard rate equations, one can obtain

$$F = 1 - \left(1 - \frac{1}{\dfrac{S_0 - 2V_0}{V_0}}\right)^{k_2/k_1}$$

where F = fraction of ^{18}O exchange found in $VO(SCN)_5^{3-}$, S_0 = initial $[SCN^-]$, V_0 = initial $[VO_2^+]$, k_2 = rate constant of oxygen exchange with solvent, and k_1 = rate constant of the VO_2^+–SCN reaction. Using $k_{obsd}(SCN^-\text{ reduction}) = 40$ s^{-1} and $[SCN^-] = 5$ M gives $k_1 = 8.0\ s^{-1}\ M^{-1}$. With $F = 0.86$ (approximate) and $V_0 = 0.13$, $k_2 = 4.7\ s^{-1}$ ($t_{1/2} = 0.15$ s). Thus, the overall specific rate constant of oxygen exchange on VO_2^+ of about 5 s^{-1} is consistent with the results under (a)

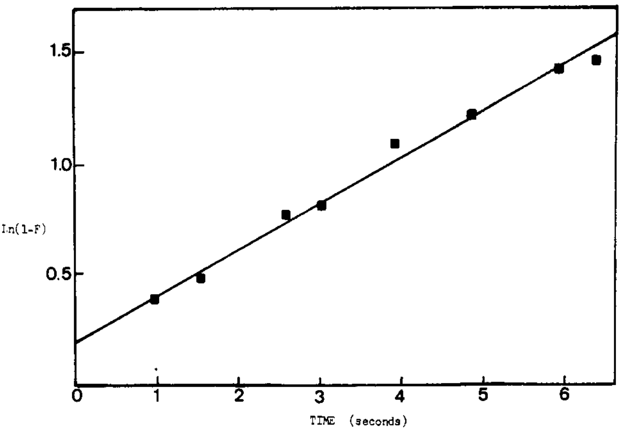


Figure 1. Representative kinetic plot for the $VO_2(C_2O_4)_2^{3-}$–H_2O exchange.

with $[VO_2(C_2O_4)_2]^{3-}$ as the sampling ion. While this result is quite imprecise, it represents the first estimate of this rate. The $t_{1/2}$ is thought to be a lower limit, estimated to be accurate to within a factor of 3.

c. $[VO_2(C_2O_4)_2]^{3-}$–$H_2{}^{18}O$ Exchange Kinetics. The exchange was found to exhibit first-order behavior by following the McKay equation as shown in Figure 1. Thus no chemical reaction occurs during the exchanging period, a conclusion that was anticipated due to the large formation constants[12] and the lack of visible oxidation–reduction when the complex is free of excess $C_2O_4^{2-}$. The graph of $-\ln(1 - F)$ vs. time was linear to at least 90% completion, but there was a constant zero-time intercept, which was judged to be due to the time necessary for precipitation and to some exchange with the solid. Neither of these could be modified significantly although the time of solid–solute contact was minimized and held constant. On the basis of the oxygen isotopic content of the solid complex, that of the initial and final solvent, and that of the nonexchanging oxalate oxygens, the number of exchanging oxygens per vanadium was calculated to be 2.0 ± 0.1 (five values).

Initial yl-oxygen exchange rate experiments gave an observed half-time of about 2 s at 0 °C and a pH of 4.6 with an estimated error of 10–15%. The possibility of V(IV) catalysis by impurities was checked early in the study by adding 10^{-3} M $H_4IO_6^-$ to the vanadium complex solution 1 h before beginning the exchange study. This was shown to be ample time for complete oxidation of VO^{2+} and $VO(C_2O_4)_2^{2-}$ in the neutral region. It was also shown that $H_4IO_6^-$ slowed the apparent exchange rate constant to about 0.21 s^{-1} ($t_{1/2}$ = 3.3 s). Both $H_4IO_6^-$ in differing concentrations and CrO_4^{2-} gave this lower rate while H_2O_2 and O_2 were only partially effective. The presence of free $C_2O_4^{2-}$ also slowed the observed specific rate to the constant value, presumably by complexing traces of VO^{2+}. Finally, catalysis was observed when $VOSO_4$, but not $[VO(C_2O_4)_2]^{2-}$, was added in small amounts. Table III gives the results of these rate studies. Other factors such as using Pt instead of stainless-steel needless for transfer and injection, laboratory light, air vs. N_2 atmosphere, or different complex preparations did not influence the rate in the presence of $H_4IO_6^-$. With the rate of exchange assumed to be first order in complex

$$k[\text{complex}] = \text{rate} = k_{\text{obsd}} \times 2[\text{complex}][H_2O]/2[\text{complex}] + [H_2O]$$

which was found to be the case and since $[H_2O] >> 2$[complex], k_{obsd} should be independent of [complex] and equal to $^1/_2k$. Therefore, the specific rate is 0.42 ± 0.04 s^{-1} at 0 °C and pH 4.6.

Table III. $VO_2(C_2O_4)_2^{3-}$–$H_2{}^{18}O$ Exchange

run	oxidant	[complex], M	k_{obsd},[a] s^{-1}
1		0.251	0.31
2		0.247	0.32
3		0.370	0.31
4		0.222	0.28
5	0.0014 M $NaIO_4$	0.170	0.21
6	0.0010 M $NaIO_4$	0.183	0.21
7	0.0004 M $NaIO_4$	0.183	0.23
8	0.0013 M $K_2Cr_2O_7$	0.200	0.22
9	0.0020 M $K_3C_2O_4$	0.211	0.21
10	O_2 (air)	0.182	0.24
11	O_2 (air)	0.183	0.26
12[b]	O_2 (air)	0.183	0.25
13	O_2 (air)	0.185	0.26
14	H_2O_2	0.208	0.26
15[c]	10^{-3} M $NaIO_4$	0.346	0.20
16[d]		0.135	0.25
17[d]		0.173	0.25
18[d]		0.165	0.26
19[d]		0.181	0.35
20		0.193	0.25

[a] At 0 °C; pH ~4.6. [b] Vanadium solution from run 11 was allowed to set for 3 days without continued aeration. [c] Platinum needle used for all solutions. [d] For runs 16 and 19, 2.8×10^{-4} and 1.7×10^{-3} M $VOSO_4$ was present, respectively. For runs 17 and 18, 2.8×10^{-4} and 1.7×10^{-3} M $Cs(NH_4)[VO(C_2O_4)_2]$ was present, respectively.

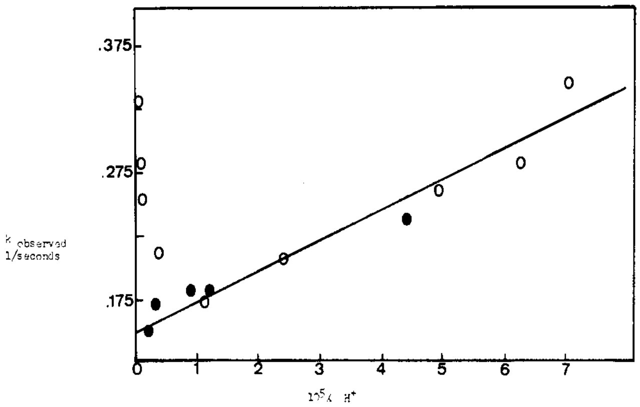


Figure 2. Acid dependence of the $VO_2(C_2O_4)_2^{3-}$–H_2O exchange: ○, normal runs; ●, pH equilibrated before initiation (least-squares line, excluding "normal runs" below pH 5).

The velocity of this reaction was so high that any significant increase in temperature would have put it out of the range of our method, and so temperature dependence studies were not made.

The pH dependency is complicated by a slow chemical reaction that changes the structure of the complex ion in the more basic region and releases oxalate ion. Figure 2 shows a sensibly linear relationship over the pH range 3.7–5.6 for runs that either had a pH <4.5 or were given time to equilibrate before exchange was begun. All runs contained $H_4IO_6^-$. However, the composition of the precipitated complex ion was not altered nor was the ∞ value, which is sensitive to the ratio of exchanging oxygens/total oxygens in the solid. From Figure 2 one can describe k_{obsd} as $k_{\text{obsd}} = k_0 + k_h[H^+]$ and the values $k_0 = 0.15$ s^{-1} and $k_h = 2.3 \times 10^3$ M^{-1} s^{-1} emerge. Table IV shows that the rate increased with increasing salt concentrations (with the nature of the positive ion being important) and that $[C_2O_4^{2-}]$ had no effect. In 65% MeOH the rate decreased while D_2O increased the rate.

d. $[VO_2(EDTA)]^{3-}$–H_2O Exchange. Difficulty was encountered in finding a precipitating agent for the ion that was not hydrated. $UO_2^{2+}(aq)$ gave reasonable results, but scatter of the data points was obvious. Nevertheless, it seems rea-

---

(12) Stary, J. *Anal. Chim. Acta* **1963**, *28*, 132.

Table IV. $VO_2(C_2O_4)_2^{3-}$–$H_2^{18}O$ Exchange

pH	k_{obsd},[a] s^{-1}	pH	salt addition	k_{obsd},[a] s^{-1}
3.7	0.40	6.0		0.34
3.8	0.42	5.4[c]		0.23
4.15	0.35	5.4[d]		0.19
4.2	0.29	5.4[d]		0.21
4.3	0.26	3.8[c]		0.26
4.35[d]	0.24	4.6	0.0538 M CsCl	0.21
4.6	0.21	4.6	0.0547 M KNO_3	0.23
4.9[b]	0.19	4.6	0.313 M $K_2C_2O_4$	0.22
4.95	0.17	4.6	0.0534 M $NaNO_3$	0.25
5.05[b]	0.18	4.6	0.0542 M NaCl	0.24
5.45[b]	0.18	4.6	0.0533 M $LiNO_3$	0.18
5.6[b]	0.15	4.6	0.0767 M $LiNO_3$	0.17
5.4	0.21	4.6	0.0226 M KNO_3	0.30
5.8	0.26	4.6[e]	0.0669 M KNO_3	0.33
5.9	0.29		65% MeOH	0.15
			13% D_2O	0.27

[a] At 0 °C; [complex] = 0.19 M; $[NaIO_4] = 10^{-3}$ M. [b] Complex solution equilibrated at given pH prior to addition of $H_2^{18}O$; otherwise, acid or base added with $H_2^{18}O$. [c] No IO_4^- present. [d] Oxidized with air (24 h). [e] No oxidant present; $k_{obsd} = 0.31\ s^{-1}$ with no KNO_3.

sonable to report the values obtained since their magnitude is correct and can be compared with those of the other systems studied. UO_2^{2+} was in water of the same ^{18}O content as the exchanging mixture and in runs 1 and 2 was equilibrated for 2 min and 2 h, respectively, before use. The values for k_{obsd} from McKay plots were $(1.4 \pm 0.3) \times 10^{-2}$ and $(1.0 \pm 0.3) \times 10^{-2}\ s^{-1}$ respectively, the same within experimental error at a pH of 7.0 and 0 °C.

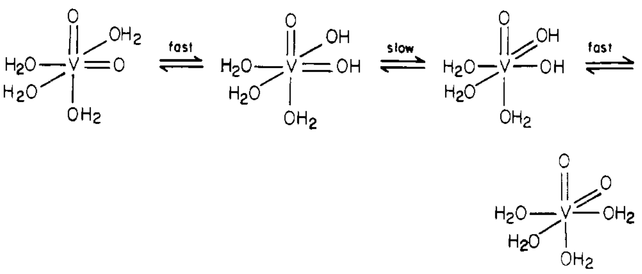
Discussion

Our attempts at measuring the VO_2^+–H_2O exchange rate have shown it to be fast and to be out of the range of conventional static methods. Though the rate of VO_2^+ exchange as measured by the competition method is not accurate, it does suggest that the rate is within the range of NMR measurements using ^{17}O.

It is rather astonishing that this observed rate is so great compared to the other di-yl-oxy ions (usually d^2) studied. The two causes for this rapidity that suggest themselves are d^0 vs. d^2 configuration or the cis structure in VO_2^+. These are interrelated however since a d^2 configuration favors the *trans*-dioxo structure and the d^0 situation favors a *cis*-dioxo arrangement. Although VO_2^+ at present is the only example, it appears that d^0 or a *cis*-dioxo structure leads to rapid oxy–H_2O exchange. This point plays a significant part in the suggested mechanism.

The estimated rate constant for exchange may be significantly in error due to our assumptions. If oxygen retention upon V(V) to V(IV) reduction is not quantitative, if V(IV) catalysis of the VO_2^+–H_2O exchange is appreciable, or if VO_2^+–H_2O exchange is enhanced by NCS^- or ox^{2-} complexation, then the observed rate would be greater than the actual rate and the half-time estimated would be a lower limit. It should be noted however, from the ox^{2-} and $EDTA^{4-}$ complex exchange studies, that ligands other than water in the equatorial positions reduce the rate. The first reaction of NCS^- with VO_2^+(aq) is expected to be NCS^- substitution for H_2O in the equatorial positions, followed by reduction. If the latter reaction is roughly equal in velocity to the first, the observed exchange rate would be that of VO_2^+(aq), but if the latter reaction is slower than complex formation, then the rate observed would be for an average $VO_2(NCS)_n^{1-n}$ complex ion. In any event, the presence of NCS^- in the coordination sphere should alter the rate by less than a factor of 2 or 3. This effect would however make the observed rate smaller than that of VO_2^+(aq).

Scheme I

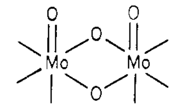


When VO_2^+(aq) is complexed with ox^{2-} (*cis*-$[VO_2(ox)_2]^{3-}$), the oxygen-exchange rate for this complex follows the equation

$$\text{rate} = k_0[\text{complex}] + k_h[\text{complex}][H^+]$$

($k_0 = 0.31 \pm 0.10\ s^{-1}$, $k_h = (4.7 \pm 0.1) \times 10^3$ at 0 °C). For a reaction with oxo-dissociative character one would expect k_0 for $VO_2(ox)_2^{3-}$ to be larger than that for VO_2^+(aq) on the basis of charge. For a reaction with considerable associative character, little change in rate would be expected. A more reasonable mechanistic picture gives unique characteristics to water in the equatorial position(s): in particular, an internal electronic rearrangement (IER) resulting in an yl position being transferred to another octahedral position assisted by proton transfers involving the solvent. Since the coordinated waters are very fast to exchange, this effectively gives yl-oxygen exchange. (See Scheme I.) Such an electronic change (with concurrent H^+ transfers) would only be possible if water(s) were in the remaining positions. With $VO_2(ox)_2^{3-}$, exchange by this mechanism could occur, although more slowly, through partial dissociation of one end of an ox^{2-}. Thus the rate of exchange would be related to the extent of one-ended dissociation of the polydentate ligand and to the formation constant of the complex. The slow exchange of the $EDTA^{4-}$ complex, $k_0 = 0.014\ s^{-1}$, is anticipated due to the greater stability of its complex, its ability to coordinate to all non-yl positions, and to the lower tendency to have species containing water in the coordination sphere. Enhancement of the ^{18}O exchange in *cis*-$VO_2(ox)_2^{3-}$ by acidity and, to a smaller extent, by larger positive ions would be expected due to their ability to stabilize the half-bonded intermediate or the mono(oxalato) complex, both of which would have coordinated water.

The validity of the IER mechanism is supported by the similar kinetic exchange behavior of VO^{2+}.[4] That the mechanism may have more general application is suggested by the available data[13,14] on the complex ions of Mo(V), $Mo_2O_4^{2+}$, $[Mo_2O_4(\text{cysteine})_2]^{2-}$, and $[Mo_2O_4(EDTA)]^{4-}$. In these complexes the



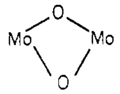
structure persists and the yl oxygens are the faster to exchange in the simple aquo ion. Tying up the water positions with cysteine ligands results in slow exchange (only the bridging oxygens exchange). Thus yl-oxygen exchange seems to require a water in an adjacent position. No exchange is seen for the EDTA complex over reasonably long periods over a wide pH range. Apparently EDTA prevents yl exchange by replacing all adjacent waters and almost stops bridging oxygen exchange by preventing

---

(13) Landis, C. R.; Robinson, P. R.; Murmann, R. K.; Haight, G. P. *Chem. Uses Molybdenum, Proc. Int. Conf., 3rd* **1979**, 249.

(14) Unpublished results: Rodgers, K. M.S. Thesis, University of Missouri, 1982.

Inorg. Chem. **1983**, *22*, 1077-1081 **1077**



ring opening.

In order for the IER mechanism to operate on *trans*-dioxo ions a *cis*-dioxo intermediate state would be necessary. So in *trans*-dioxo systems, high activation energies are expected, resulting in a lower rate or in the intervention of another mechanism. Thus, in spite of the tendency for weakening the yl-metal bond in the trans ions due to the trans effect, the rate of yl-oxygen exchange is generally considerably slower than in cis ions.

It is significant that rapid electron exchange between $[VO_2(ox)_2]^{3-}$ and $[VO(ox)_2OH_2]^{2-}$ does not occur as evidenced by the lack of catalytic effect of the latter on the oxygen exchange of the former. This may be due to the different geometry since the V(V) complex is cis while with V(IV) the O and OH_2 are trans. Most *trans*-dioxo ions are d^2 ions, which strongly favors the trans configuration, making the cis form thermodynamically unstable.

Conclusions

The rate of yl-oxygen exchange of $VO_2^+(aq)$ with water in acid solution has a half-time of about 0.15 s at 0 °C. Complexation causes a lowering of the rate: $VO_2^+(aq) > [VO_2(ox)_2]^{3-} > [VO_2(EDTA)]^{3-}$. An internal rearrangement mechanism is suggested as the basic mechanism by which yl-oxygen exchange occurs for *cis*-dioxo complexes.

Acknowledgment. The authors express their appreciation to the University of Missouri Research Council for partial support of this work.

Registry No. O_2, 7782-44-7; VO_2^+, 18252-79-4; $VO_2(C_2O_4)_2^{3-}$, 56556-47-9; H_2O, 7732-18-5; SCN^-, 302-04-5; $VO_2(EDTA)^{3-}$, 68907-94-8.

Contribution from the Department of Chemistry,
Schlundt Hall, University of Missouri, Columbia, Missouri 65201

Bis[3-(hydroxyamino)-3-methyl-2-butanone oximato(2–)-*N*,*N'*]nickel. Structure and Properties of a $[Ni(DMG)_2]^0$-Related Complex

E. O. SCHLEMPER and R. KENT MURMANN*

Received July 21, 1982

A unique, planar, nickel complex, $[Ni(HAO)_2]^0$, $NiC_{10}H_{20}N_4O_4$, has been prepared, which formally contains Ni(IV) and two doubly deprotonated α-hydroxyamine oxime, 3-(hydroxyamino)-3-methyl-2-butanone oximate(2–) (HAO), ligands. It is extremely planar, deeply purple (ϵ = 3050 M^{-1} cm^{-1}, λ_{max} = 5410 Å), and quite soluble in organic solvents but slowly decomposes in solution. The X-ray study shows a monoclinic cell ($P2_1/c$) with a = 6.400 (2) Å, b = 9.333 (1) Å, c = 11.736 (1) Å, β = 90.37 (2)°, and Z = 2. The X-ray crystal structure shows it to be very similar to $[Ni(DMG)_2]^0$ with an extra CH_3 group on one of the ring carbons, which prevents one of the $-C{=}N{-}OH$ multiple bonds of the DMG complex. The molecule has a center of symmetry, intramolecular O–H···O hydrogen bonds, and two very short Ni–N bonds (1.804 (2) Å). Delocalized multiple bonding is indicated through the O–N_{HA}–Ni–N_{HA}–O chain, (HA = hydroxyamine). The bonding in this molecule is discussed in terms of a five-atom conjugated chain (O–N–Ni–N–O) with π overlap utilizing p_z orbitals of two O and two N atoms and the d_{xz} orbital of Ni(II). It could as well be described as a square-planar, diamagnetic, deprotonated hydroxylamine oxime Ni(IV) complex. The ligand can be removed from the metal ion instantaneously with dilute acid and regenerated (~70%) with base, showing the ligand to be capable of independent existence and suggesting that other complexes of this ligand may be prepared.

Introduction

Nickel(II) complexes of aliphatic α-amine oximes are always[1] yellow-orange planar ions with small extinction coefficients ($\epsilon \approx$ 200 M^{-1} cm^{-1}, $\lambda_{max} \approx$ 4000 Å) in the visible region. During the preparation of two of these species with potentially tridentate ligands, it was noted that deep purple, water-insoluble nickel complexes were produced upon air oxidation in basic media. Spectral, elemental, and magnetic measurements showed the two purple products to be identical and indepenent of the reacting ligand.

An X-ray analysis of a single crystal, representative of the bulk samples, showed the neutral molecule to be very similar to $[Ni(DMG)_2]^0$ but with one additional methyl group on each ligand. The ligand also resembles the anticipated tridentate amine oxime ligand with bond breakage at the C–N bond of the diamine, presumably through oxidation.

This paper presents our investigation and conclusions on the method of preparation, the structure, the nature of the bonding, and the solution properties of this unique molecule. Also suggested are methods of metal ion exchange to give other metal ion complexes of the ligand that might have unusual properties.

Experimental Section

Preparation of the Complex.[2] The starting ligands were prepared from $(CH_3)_2C(Cl){-}C(CH_3){=}NOH$ and a diamine (either $NH_2C(CH_3)_2CH_2NH_2$ or $NH_2CH(CH_3)CH(CH_3)NH_2$) by refluxing the mixture having a 2:1 molar ratio of the two compounds in absolute methanol for 6 h. The product was isolated in the usual manner[2] and reacted with a slight excess of $NiCl_2$. The addition of Na_2CO_3 to free the amine and allow complexation gave a yellow-brown solution, which was filtered and aerated. The pH at this point was between 6.5 and 7.0. Gradually a deep purple solid formed, which was collected on a filter, washed with small quantities of ethanol, and recrystallized several times from acetone by the addition of water. Final crystallization is best accomplished thermally from acetone or CH_3CN. The yield averaged about 10% of the theoretical yield. Anal. Calcd for $NiC_{10}H_{20}N_4O_4$ (fw = 318.99): C 37.66; H, 6.32; N 17.57. Found: C, 37.79; H, 6.38; N, 17.54. The intensely purple diamagnetic complex is soluble in most organic solvents but is especially insoluble in water. It decomposes slowly in all solvents to a brown paramagnetic complex of unknown structure. The complex is changed to a colorless species

---

[1] Murmann, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 521; **1962**, *84*, 1349.

[2] Murmann, R. K. *J. Am. Chem. Soc.* **1958**, *80*, 4174.

0020-1669/83/1322-1077$01.50/0 © 1983 American Chemical Society