is observed, which drops to 7 ppm for the tributoxide derivatives. The strong back-bonding ability of the NO ligand in the molybdenum complex may account for the larger shift with that molecule. The usefulness of this parameter to measure the degree of M–O multiple bonding needs further investigation.

The fluxional behavior of the three $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ (R = H, *i*-Pr, *n*-Bu) complexes can reasonably be explained by a number of possible mechanisms. The first is dissociation of one of the pz rings from coordination to the metal and rapid rearrangement of the five-coordinate intermediate thus produced, followed by reassociation of the free pz ring. Although no direct demonstration of this sequence has been observed, the equilibration of the fourth pz ring in complexes such as $[B(pz)_4]Pd(\eta^3\text{-}C_3H_5)$[9] or $[B(pz)_4]Cu(CO)$[10] must require the dissociation step and five-coordinate molecules are well-known to have a low barrier to rearrangement.[11]

The second mechanism is a simple rotation of the pyrazolylborate ligand about the Zr–B axis, a trigonal-twist mechanism. That this mechanism is most likely to be correct was demonstrated by the study, shown in Figures 3 and 4, on $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$. In this case, if the dissociative mechanism was correct, the fluxional process would equilibrate all four pz rings. This is not the case. A similar trigonal-twist mechanism was shown earlier for $[B(pz)_4]Mo(CO)_2(\eta^3\text{-allyl})$ complexes,[6a] where the barrier was calculated for a number of complexes to be ca. 14 kcal mol^{-1}. A similar process was also proposed for $[B(pz)_4]Pt(CO)CH_3$,[6b] where the barrier was measured to be 10.5 kcal mol^{-1}. Our measured barrier of 13.4 kcal mol^{-1} for $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ is in this same range. These studies represent the first investigation of this type of fluxional behavior for discrete six-coordinate complexes. On the basis of 60-MHz ^1H NMR data, the molecules $[B(pz)_4]Mn(CO)_2PR_3$ (R = OMe, Me) were reported to be fluxional at 5 °C but solubility problems prevented a low-temperature study.[12] From the spectrum of $[B(pz)_4]Mn(CO)_2P(OMe)_3$ pictured in this paper, the interpretation of fluxional behavior at 5 °C is questionable. In fact, this spectrum more closely matches our low-temperature spectrum for $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ than the high-temperature spectrum. Higher field ^1H or ^{13}C NMR data are needed to conclusively prove this point. Numerous other six-coordinate complexes, mainly of molybdenum (e.g., $[RB(pz)_3]Mo(CO)_2(N_2Ph)$[13a]), show static NMR spectra at room temperature.[4,13]

A final reasonable mechanism would be dissociation of either a Cl or an O-*t*-Bu ligand and rapid rearrangement of the five-coordinate species thus produced, followed by reassociation of the ligand. Two points argue against this type of mechanism. First, these molecules are 12-electron species and should be reluctant to dissociate a ligand, particularly the O-*t*-Bu ligand in which multiple M–O bonding is likely. Second, and more important, is the fact that the complex $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ is not fluxional up to 140 °C. Dissociation of a ligand from this more sterically hindered molecule (this ligand should also be a better electron donor) would be expected to be a lower energy process, not higher as observed. One can easily explain the higher barrier for this molecule if the trigonal-twist mechanism is correct in that the 3-Me (pz) groups would seemingly lock like gears with the O-*t*-Bu and Cl ligands, hindering the rotation.

Acknowledgment. We wish to thank Dr. Ron Garber and Mr. Neil Swift for assistance in obtaining the computer-simulated NMR spectra and Mr. Michael Walla for the computer-simulated mass spectral data.

Registry No. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-13-6; $[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-14-7; $[n\text{-}BuB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-15-8; $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_3$, 84695-16-9; $[i\text{-}PrB(pz)_3]Zr(O\text{-}t\text{-}Bu)_3$, 84695-17-0; $[B(pz)_4]ZrCl_3$, 84695-18-1; $[HB(pz)_3]ZrCl_3$, 84695-19-2; $[HB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-20-5; $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-21-6; $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$, 80041-67-4; $[i\text{-}PrB(pz)_3]ZrCl_3$, 80041-70-9; $[n\text{-}BuB(pz)_3]ZrCl_3$, 80041-69-6; $K[B(pz)_4]$, 14782-58-2; $Na[HB(pz)_3]$, 18583-62-5.

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Isotopic ^{18}O Exchange between $VO^{2+}(aq)$ and Water

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The intrinsic rate of yl-oxygen exchange ($t_{1/2}$ = 400 min at 0 °C) of $VO^{2+}(aq)$ with solvent water follows the rate law rate = $k_0[VO^{2+}(aq)] + k_{OH}K_{eq}[VO^{2+}(aq)]/[H^+]$ with $k_0 = (2.4 \pm 0.8) \times 10^{-5}$ s^{-1}, $k_{OH} = 1.32 \pm 0.11$ s^{-1}, and $K_{eq} = 3.98 \times 10^{-7}$ M at 0.0 °C and $I = 2.54$. At $[VO^{2+}] = 0.18$ M, $I = 0.64$, and $[H^+] = 0.10$ M as chloride salts, $\Delta H^* = 20.5 \pm 1.1$ kcal/mol and $\Delta S^* = -4.4 \pm 0.2$ cal/(mol deg). The exchange is catalyzed by VO_2^+, giving a $k_{VO_2^+}$ of 3.91 ± 0.09 M^{-1} s^{-1} at 0.0 °C, $[H^+] = 0.1$ M, and $I = 0.37$. $[VO(NCS)(OH_2)_4]^+$ exchanges with $k_{NCS} = (5.56 \pm 0.14) \times 10^{-7}$ M^{-1} s^{-1} at 0.0 °C and $I = 0.7$, considerably lower than the parent aquo ion. When complexation was by oxalate or EDTA^{4-}, the exchange rate increased with acidity and had a very small k_0 term while with NTA^{3-}, where an equatorial water was probably present, the faster rate was inversely related to the acidity.

Introduction

In recent years a knowledge of the aqueous structure and rates of solvent exchange with oxyions has become essential to an understanding of a host of other experimental studies including oxidation–reduction mechanisms, atom-transfer reactions, and ligand substitution processes. For oxygen exchange, processes in water that are relatively slow, static methods employing ^{18}O have proven highly successful. These studies coupled with X-ray crystal studies have led to significant progress with species such as $V_{10}O_{28}^{6-}$,[1] $Mo_2O_4^{2+}$,[2] and

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† Submitted in partial fulfillment of the requirements for the M.A. degree, 1981.

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Te(OH)$_6$,[3] and the basic structure of the Mo(IV) species was shown to be a trimer Mo$_3$O$_4$(OH$_2$)$_9$$^{4+}$.[4] It now appears that most yl-type oxygens and many bridging oxygens exchange slowly enough with solvent water to be studied by this technique.

It has long been "known" from extension of solid X-ray structural studies[5] that aqueous acidic V(IV) contains a multiply bound yl-type (oxo) oxygen with a V–O distance of about 1.6 Å. Also present are four equatorial waters at about 2.0 Å, which exchange with solvent rapidly ($k \sim 5 \times 10^2$ s^{-1})[6] at 25 °C. An axial water is found at about 2.4 Å and exchanges extremely rapidly.[6] In a preliminary study on the V(IV) system it was shown that the $t_{1/2}$ for exchange of the VO^{2+}(aq) oxygen was about 300–400 min at 0 °C in acidic media, but the precision of the methods employed did not allow a serious evaluation of the rate law or the effects of solution environmental changes.[7]

This paper reports a more precise new method for determining the isotopic composition of the vanadyl oxygen, which is applied to the aquo ion and four of its complexes (C$_2$O$_4$$^{2-}$, NCS$^-$, NTA^{3-}, EDTA^{4-}) in an effort to establish the mechanistic process by which a solvent molecule interchanges with the vanadium(IV) oxygen.

Experimental Section

Stock solutions of VOCl$_2$, which were nearly neutral (pH ~4), were prepared either by precipitation of BaSO$_4$ from recrystallized VOSO$_4$ (hydrate) with a BaCl$_2$ solution or, more often, by reduction of acidic (HCl) V$_2$O$_5$ with a slight excess of hydrazine. Both preparations gave VO^{2+}(aq) solutions with the same exchange properties. When ^{18}O-enriched, the solvent was equilibrated with the vanadyl salt for over 1 day at room temperature. Cl$^-$ coordination to VO^{2+}(aq) is relatively small: $K = 0.38$, $I = 1.1$, $T = 19$ °C.[8]

Solid (CH$_3$)$_4$N$^+$NCS$^-$ was prepared by saturating a Dowex 1-X4 resin with NCS$^-$, passing a dilute solution of (CH$_3$)$_4$N$^+$Br$^-$ over it, and collecting the effluent. After tests for the absence of bromide, the solution was evaporated to dryness at about 30 °C in a rotoevaporator under vacuum and stored in a desiccator.

(NH$_4$)$_2$[VO(C$_2$O$_4$)$_2$OH$_2$]·H$_2$O was prepared following the method of Koppell and Goldmann.[8] It was recrystallized as the CsNH$_4$[VO(C$_2$O$_4$)$_2$OH$_2$]·H$_2$O salt. The oxalate ion is very tightly held, and Ba^{2+} produces no BaC$_2$O$_4$(s) upon standing overnight. Anal. Calcd for CsNH$_4$[VO(C$_2$O$_4$)$_2$OH$_2$]·H$_2$O (fw = 430): C, 11.17; H, 1.88. Found: C, 11.76; H, 2.08.

((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$] was prepared by adding an excess of (CH$_3$)$_4$N$^+$NCS$^-$ to a solution of VO^{2+}(aq). The dark blue precipitate immediately obtained was freed of solvent by centrifugation, washed first with 1-propanol and then with diethyl ether, and vacuum dried. Anal. Calcd for ((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$] (fw = 579): C, 34.49; H, 6.13; N, 18.93. Found: C, 35.33; H, 6.20; N, 19.36.

[VO(NTA)OH$_2$]$^-$ and [VO(EDTA)]$^{2-}$ were prepared in solution by adding the appropriate amount of ligand into a standardized VOCl$_2$ solution and adjusting the pH to the desired value. The structure of these ions in solution had been previously determined by Connick.[9]

Water used in these studies was distilled and treated with a double-bed ion exchanger. The ^{18}O water was from Bio-Rad and was normalized with respect to deuterium. Chemicals for ionic strength control and for complex preparation were of reagent grade.

The new method for determining the ^{18}O content of VO^{2+} involved the rapid formation of VO(NCS)$_5$$^{3-}$ and crystallization as anhydrous ((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$]. One milliliter of a 0.2 M VO^{2+}(aq) solution was treated with 1.0 mL of a saturated (CH$_3$)$_4$N$^+$NCS$^-$ solution at 0.0 °C. The resulting fine blue powder was collected by centrifugation, washed three times with cold 1-propanol, followed by two washings with anhydrous diethyl ether, and dried in a stream of nitrogen. After evacuation at 10^{-4} mmHg for 12 h, it was converted to CO$_2$, which was purified and analyzed for ^{18}O content. Conversion to CO$_2$ was accomplished by heating to 375 °C for 2 h with HgI$_2$ in a sealed tube.[10] The gaseous contents of the tube with no appreciable vapor pressure at liquid-nitrogen temperatures were separated by VPC over silicone oil on firebrick at 25 °C, and CO$_2$ was quantitatively collected for analysis. A Nuclide RMS mass spectrometer was used to measure the 46/(44 + 45) ratio, R, which was normalized, R_n, to an arbitrary value of 4.00 × 10^{-3} for a standard normal sample of CO$_2$. An estimation of the percent induced exchange for enriched VO^{2+}(aq) in normal water caused by the chemical change and separation procedure gave about 5%. Reproducibility was found to be within 2%.

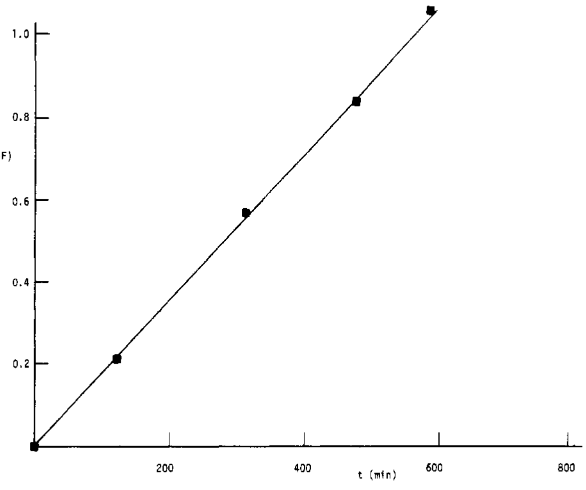

Figure 1. Rate of ^{18}O exchange of VO^{2+}(aq) at 0 °C, [VO^{2+}] = 0.18 M, [H$^+$] = 0.1 M, and I = 0.64 (NaCl).

For a kinetic study of the VO^{2+}(aq)–H$_2$O exchange rate, about 450 μL of an ^{18}O-enriched vanadyl solution containing a slight excess of hydrazine was injected into 4.5 mL of 0.1 M HCl containing 50 μL of 0.09 M hydrazine. All reagents were previously cooled at 0.0 °C and held there by a water–ice slurry. At timed intervals, 1.0-mL aliquots were removed and immediately converted to ((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$], which after careful drying was converted to CO$_2$.

Graphs of ln $[(R_0 - R_\infty)/(R_0 - R_t)]$ vs. time were linear for 4 half-lives, and k_{obsd} was obtained from the slope of the linear least-squares line. The rate was found to be first order in [VO^{2+}(aq)] from concentration studies and thus

$$k[\mathrm{VO}^{2+}] = R = k_{\mathrm{obsd}}\left(\frac{ab}{a+b}\right)$$

where a = [VO^{2+}] and b = [H$_2$O]. On the assumption $a + b = b$, it follows that $k_{obsd} = k$.

The NCS$^-$ complex exchange was investigated by adding known amounts of NaNCS to 2 mL of an unenriched vanadyl stock solution containing a trace of hydrazine. One-half milliliter of 1 M HCl was added and the total volume brought up to 4.0 mL with deionized water. All solutions were held at 0.0 °C in an ice slurry. One milliliter of enriched ^{18}O water was injected, and 1.0-mL aliquots were withdrawn at timed intervals and precipitated as ((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$], which was subsequently converted to CO$_2$ for analysis.

For the oxalato complex, a 0.2-g sample of (NH$_4$)$_2$[VO(C$_2$O$_4$)$_2$OH$_2$]·H$_2$O was dissolved in 4.0 mL of deionized water, the pH was adjusted with 12 M HCl or solid NaOH, and the solution was cooled to 0.0 °C in an ice bath. One milliliter of enriched water was added and the mixture sampled at timed intervals. The sampling technique differed from that of the aquo ion because no adequate precipitating agent for [VO(C$_2$O$_4$)$_2$OH$_2$]$^{2-}$ could be found. Thus the oxalate complex was rapidly converted to VO^{2+}(a) at 0.0 °C by the addition of concentrated HCl. Then ((CH$_3$)$_4$N)$_3$[VO(NCS)$_5$] was precipitated in the previously described fashion. Likewise for the NTA^{3-} and

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(10) The usual method utilizes HgCl$_2$–Hg(CN)$_2$ mixtures (or HgCl$_2$ only when organic carbon is present) and 425 °C for 1 h. With compounds containing small amounts of oxygen, large samples are needed and the usual method results in excessive pressures of HCl and a large fraction of explosions. Using HgI$_2$(anhydrous) and a slightly lower temperature increases the probability of obtaining satisfactory CO$_2$ samples without significantly decreasing the yield.

Table I. Comparison of the VO^{2+}-H_2O Exchange Rate by Different Methods

method	$t_{1/2}$, min	$10^6 k_{obsd}$,[a] s^{-1}
H_2O[b] (evap)	402	2.87 ± 0.34[d]
F^-[b] (ppt)	374	3.09 ± 0.15
TMAT[c] (ppt)	411	2.81 ± 0.17

[a] T = 0 °C; [HCl] = 0.1 M. [b] Previous work;[7] Fe(II) present. [c] Traces of hydrazine present (see text). [d] The ± values throughout the study are one standard deviation from the linear least-squares treatment of the data.

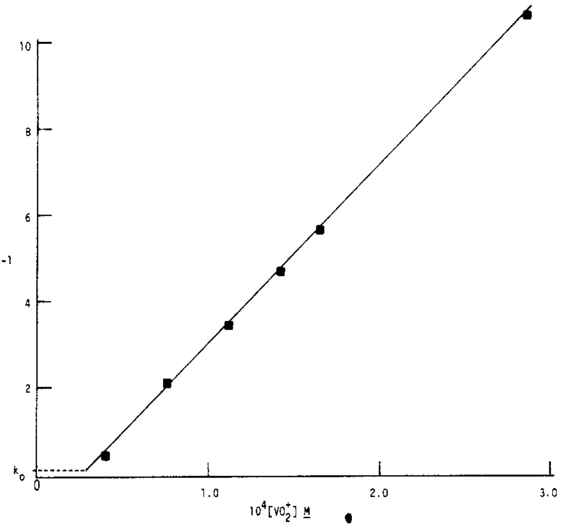

Figure 2. Effect of VO_2^+ on VO^{2+} oxygen exchange at 0 °C, [H^+] = 0.1 M, and I = 0.37 (NaCl).

$EDTA^{4-}$ complexes, isotopic analysis was accomplished by converting to VO^{2+}(aq) and precipitating as the thiocyanate complex.

Results

The new experimental method of ^{18}O analysis in VO^{2+}(aq) utilizing $(CH_3)N^+NCS^-$ (TMAT) is much more convenient and gives higher internal precision than the previous methods. A typical McKay graph is given in Figure 1. Table I compares the three methods, showing essential agreement, with the precision for TMAT (10 runs) about equal to that with F^-. The effect of light was investigated, and in normal light a rate of (2.81 ± 0.17) × 10^{-5} s^{-1} was obtained to be compared with the dark reaction rate of (2.83 ± 0.12) × 10^{-5} s^{-1} at 0 °C, [HCl] = 0.1 M, and [VO^{2+}(aq)] = 0.18 M with hydrazine present. All samples of VO^{2+}(aq) prepared were found to contain traces of V(V), which increased the apparent rate of VO^{2+}–H_2O exchange. To prevent this catalyzed exchange, stock VO^{2+}(aq) solutions contained traces of hydrazine, which was shown to reduce V(V) rapidly in slightly acidic media. Except for the V(V)-catalyzed set of experiments, all VO^{2+}(aq)–H_2O exchange studies contained excess hydrazine at the 10^{-5} M level.

A first-order dependence was found for VO_2^+ catalysis of the VO^{2+}(aq)–H_2O exchange; see Figure 2. The intercept at zero [VO_2^+]added is not k_0 due to hydrazine present in the stock solution, which consumed some of the added VO_2^+. These results are in agreement with the rate equation

$$R/[VO^{2+}(aq)] = k_0 + k_{VO_2^+}[VO_2^+]$$

where k_0 = (2.4 ± 0.8) × 10^{-5} s^{-1} and $k_{VO_2^+}$ = 3.9 ± 0.09 M^{-1} s^{-1} at 0.0 °C, [H^+] = 0.10 M, and I = 0.37 (NaCl).

The hydrogen ion effect was studied at [VO^{2+}(aq)] = 0.18 M and I = 2.5 (NaCl) at 0.0 °C. Table II shows the results over the acidity range 0.005–2.0 M. An inverse relationship sensibly exists with a reasonable fit to the expression

$$R = k_0[VO^{2+}(aq)] + k_{OH}[VO(OH)^+(aq)]$$

Table II. Effect of [HCl] on VO^{2+}–H_2O Exchange Rate

[HCl],[b] M	$t_{1/2}$, min	$10^5 k_{obsd}$,[a] s^{-1}
0.0046	85.5	13.5 ± 0.11
0.017	172	6.72 ± 0.08
0.1	461	2.51 ± 0.13
1.0	503	2.30 ± 0.07
2.0	595	1.95 ± 0.04

[a] T = 0 °C; hydrazine present. [b] I = 2.54 (NaCl); [VO^{2+}] = 0.18 M.

Table III. Positive-Ion Effects on the VO^{2+}-H_2O Exchange Rate[a]

ion	[ion], M	[H^+], M	I	$t_{1/2}$, min	$10^5 k_{obsd}$, s^{-1}
H^+	0.1	0.1	0.38	411	2.80 ± 0.17
H^+	1.0	1.0	1.28	448	2.58 ± 0.11
Li^+	0.9	0.1	1.28	507	2.28 ± 0.02
Na^+	0.9	0.1	1.28	458	2.52 ± 0.09

[a] T = 0 °C; counterion Cl^-; [VO^{2+}] = 0.11 M; trace of hydrazine present.

Table IV. NaNCS Dependence of VO^{2+}(aq)–H_2O Exchange Rate[a,b]

[NaNCS], M	I	$t_{1/2}$, min	$10^5 k$, s^{-1}	f(NCS)[c,d]
0.905	1.12	753	1.50 ± 0.07	0.879
0.452	0.66	642	1.80 ± 0.02	0.783
0.226	0.44	537	2.15 ± 0.13	0.644
0.100	0.31	425	2.72 ± 0.02	0.444

[a] [V(IV)] = 0.11 M; [HCl] = 0.1 M. [b] T = 0.0 °C; hydrazine present. [c] $f([NCS]) = K[NCS]/(1 + K[NCS])$ (see text). [d] k_1 = (3.95 ± 0.02) × 10^{-5} s^{-1}; k_{NCS} = (5.56 ± 0.14) × 10^{-7} M^{-1} s^{-1}.

On the assumption of only trace amounts of hydrolysis, the rate expression

$$R/[VO^{2+}(aq)] = k_0 + k_{OH}K_a/[H^+]$$

holds, where K_a is the hydrolysis constant of VO^{2+}(aq).[11] Using k_0 = (2.4 ± 0.8) × 10^{-5} s^{-1}, one obtains k_{OH} as 1.32 ± 0.11 s^{-1} at 0.0 °C and I = 2.5. Table III shows experiments to explore the sensitivity of the exchange rate to the presence of alkali metal ions. Only small variations were noted with the order Li^+ > Na^+ ~ H^+ in lowering the rate in a chloride ion medium. The temperature dependence in 0.1 M HCl, where the k_0 term predominates, over the temperature range 0.0–12.8 °C, at [VO^{2+}(aq)] = 0.18 M and I = 0.64 (NaCl), gave (four points) $\Delta H^\ddagger$ = 20.5 ± 1.1 kcal/mol and $\Delta S^\ddagger$ = −4.4 ± 0.2 cal/(mol deg).

In an attempt to understand the mechanism of oxygen exchange, a series of complexing ligands were used to modify the charge of the ion and to replace coordinated waters in the equatorial and/or axial positions. It is quickly apparent from a scan of the literature that quantitative information about the bonding of monodentate ligands to VO^{2+}(aq) is lacking. Thiocyanate association has been studied in some detail and only K_1 is of any importance in the [NCS^-] range of 0.1–1.0 M. The value of K_1, 8 M^{-1}, at 0.0 °C and I = 2.6, indicates that there is considerable complexation in the concentration range used.[12] Its site of coordination on the V(IV) octahedron is not known, but it is most likely coordinated through its nitrogen atom. Experimentally it is found that NCS^-, when coordinated, slows down the rate of oxygen exchange with the yl-type oxygen with little effect at the 0.1 M concentration level but increases the $t_{1/2}$ to about 750 min at 0.91 M NCS^- at 0 °C. The NCS^- effect on the rate makes the TMAT method more quantitative in that it reduces the zero-time

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Table V. VO^{2+}–H_2O Exchange Rate of Complex Ions

complex ion	pH	$t_{1/2}$, min	$10^5 k_{obsd}$,[a,b] s^{-1}
$[VO(C_2O_4)_2OH_2]^{2-}$	1.5	69	16.6 ± 5.1
	3.0	853	1.35 ± 0.1
	4.0	1100	1.07 ± 0.2
	5.0	>2 days[c]	no exchange
$[VO(EDTA)]^{2-}$	1.5	171	6.73 ± 0.1
	7.0	774	1.49 ± 0.2
	8.0	>2 days[c]	no exchange
$[VO(NTA)]^-$	3.0	37	31.6 ± 2.5
	4.2	18	63.8 ± 1.3
	6.5	2	large

[a] $T = 0.0$ °C; trace of hydrazine; $I = 0.5$. [b] ^{18}O content determined as NCS^- complex after removal of ligand by acid. [c] At 25 °C.

Table VI. Effect of Volume of HCl on Induced Exchange of $[VO(ox)_2OH_2]^{2-}$

vol of HCl added, mL	$10^3 R_{calcd}$[a]	$10^3 R_{obsd}$[c]
1.0	6.63	5.69[b]
2.0	5.75	5.51
3.0	5.31	5.57

[a] Value expected if $R_{solvent} = 9.26 \times 10^{-3}$. [b] Value low due to possible ligand contamination (see text). [c] $T = 0$ °C; $[VO(C_2O_4)_2OH_2]^{2-} = 0.1$ M; pH = 4; contact time = 30 s.

exchange. A good fit to the data of Table IV is found for the derived equation

$$R/[VO^{2+}(aq)] = k_1 + (k_{NCS}\text{-}k_1)(K_1[NCS^-]/(1 + K_1[NCS^-]))$$

where $K_1 = 8.0\ M^{-1}$, k_1 is an arbitrary constant, and k_{NCS} is defined by

$$k_{obsd} = k_0[VO^{2+}(aq)] + k_{OH}[VO(OH)^+] + k_{NCS}[VO(NCS)^+]$$

The above equations predict a linear relationship between k_{obsd} and $K_1[NCS^-]/(1 + K_1[NCS^-])$. Such was found to be the case, giving a value for k_{NCS} of $(5.6 \pm 0.1) \times 10^{-7}\ s^{-1}$ at 0.0 °C and pH 1.0.

The structures of the bis(oxalato), $EDTA^{4-}$, and NTA^{3-} complexes are better known than those of the complexes of monodentate ligands even though the latter two are prepared only in solution. Table V lists the results of the ^{18}O-exchange experiments on the yl oxygen of V(IV) when complexed by these ligands. These results are not highly accurate due to about 40–50% induced exchange during the dissociation of the complex and precipitation of $VO(NCS)_5^{3-}$. A further problem came from incomplete organic ligand removal if only 1.0 mL of concentrated HCl was used to displace the organic ligand. For $VO(ox)_2^{2-}$ (Table VI), $R_{n(obsd)}$ of $VO^{2+}(aq)$ was constant when 2–3 mL of concentrated HCl was used and differed significantly from the value $R_{n(calcd)}$ of the final solvent, showing that the ligand was completely removed and that reproducible induced exchange was encountered. In spite of these difficulties, we are confident the trends presented are characteristic of the exchange reaction being studied.

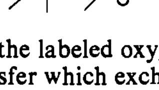
Discussion

The results of this study confirm that the half-time of water exchange with $VO^{2+}(aq)$ is the region of 400 min at 0.0 °C in the absence of traces of V(V). The report[13] that the exchange is extremely slow is probably in error, but we have no explanation for the results presented. Also, a comparison of the solvent ^{18}O content with that of the complex ion extrapolated to zero time of contact is consistent with 1.0 ± 0.1 slowly exchanging oxygens per vanadium, agreeing with the current ionic formula $VO^{2+}(aq)$. None of the three methods now available for examining the isotopic composition of the yl oxygen of $VO^{2+}(aq)$ are entirely satisfactory in that one has to deal with very high concentrations of the salt (H_2O method) or to drastically change the ion to a new complex and precipitate it (F^- and NCS^- methods). However, it is satisfying that the methods produce the same rate constant within the calculated experimental precision.

In summary, the following general features emerge: the rate of yl-oxygen solvent exchange is sensitive to (a) the presence of trace amounts of V(V) (and therefore oxidizing conditions) and (b) low acidity but is only slightly affected by the salt atmosphere and partial complexing with monodentate complexing agents. Laboratory light has no effect on the rate.

The inverse hydrogen ion dependency is best interpreted in terms of the hydrolysis of $VO^{2+}(aq)$. While not a unique interpretation, it is the most reasonable in terms of the known hydrolysis constant and the expected effect of OH^- in the coordination sphere. The ratio K_{OH}/k_0 of 6×10^4 is about what is expected for this system. In view of the fact that NCS^- in the coordination sphere has the opposite effect, one is tempted to suggest that the rapidity of the OH^- term is due to a low-energy path in which a hydroxy group in an equatorial position is converted to an yl oxygen by proton transfer to the original yl oxygen. We will call this the IER, internal electronic rearrangement, mechanism. Simple electronic weakening of the yl–oxygen bond through equatorial OH^- coordination, leading to solvent exchange on the yl oxygen would be expected to give a much smaller enhancement of the rate constant. Thus the inverse hydrogen ion dependency suggests an intramolecular yl oxygen–equatorial oxygen equivalence in the activated state. This mechanism would apply to the k_0 term as well, but with a much smaller value for k_0. For this type of mechanism, salt effects should not be large, in agreement with the observations.

Traces of either hydrazine or Fe^{2+} can be used to reduce the apparent k_{obsd} of $VO^{2+}(aq)$–H_2O exchange to a common constant value, independent of the reductant concentration, which is taken to be the intrinsic k_{obsd}. It is commonly observed that all $VO^{2+}(aq)$ solutions or salts contain small amounts of V(V). The addition of small known amounts of V(V) as $VO_2^+(aq)$ caused the exchange rate to increase linearly with $[VO_2^+]$. Extrapolation to the V(V)-free k_0 did not occur at zero V(V) added, by a finite value 2×10^{-5} M, which was consistent with the amount of free hydrazine in the stock vanadyl solution. The value for $k_{VO_2^+}$, $3.9\ M^{-1}\ s^{-1}$, while large, is completely reasonable in light of the high rate of electron exchange between the two ions.[14] In view of the like charges of the ions, K_{eq} for the formation of VO_2^+–VO^{2+} would be very small; thus $k_{VO_2^+}$ would be composed of K_{eq} and the intrinsic k for electron exchange. A direct comparison between $k_{VO_2^+}$ and k (electron exchange) cannot be made however because the latter rate expression is questionable. A reasonable picture of the activated complex (without waters) for this rate term is



which would result in the labeled oxygen occupying a VO_2^+ site after electron transfer which exchanges with the solvent at a rapid ($t_{1/2} \sim 0.2$ s) rate.[15]

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[15] Murmann, R. K.; Rahmoeller, K. M., submitted for publication in *Inorg. Chem.* Recently a mixed-valent V(IV)–V(V) complex has been observed in acidic media: Madic, C.; Blanc, P.; Launay, J. P. *Inorg. Chem.* **1982**, *21*, 2923.

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.

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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.

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

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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

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