

(bpy)₂Cl₂ (0.50 mmol dm⁻³) under otherwise identical conditions, not only HCOO⁻ (13.4 μmol) but also CO (47.2 μmol) was produced without accompanying H₂ evolution. Although the amounts of HCOO⁻ and CO formed are small compared with those produced in the catalytic system composed of [Ru(bpy)₃]²⁺

and [Ru(bpy)₂(CO)₂]²⁺ (Figure 5), the mole ratios of CO to HCOO⁻ are essentially consistent for both systems. Thus, the selectivity for CO and HCOO⁻ is mainly controlled by the medium rather than the difference between Ru(bpy)₂Cl₂ and [Ru(bpy)₂(CO)₂]²⁺.

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Vanadium-Mediated Oxygen Atom Transfer Reactions

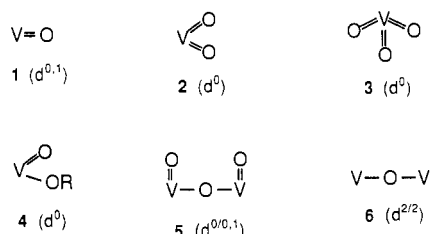
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Oxygen atom (oxo) transfer reactions mediated at vanadium centers in oxidation states II-V have been demonstrated by using the set of complexes VCl₂(py)₄, [VCl₄(MeCN)₂]⁻, VOCl₂(py)₂, [VOCl₄]²⁻, [VOCl₄]⁻, and [VO₂Cl₂]⁻ and oxo donors/acceptors XO/X in acetonitrile solutions. This set should reflect the inherent reactivity of a given oxidation state in a somewhat conserved ligand environment, without undue ligand effects on reactivity. The following transformations have been proven, either by product isolation in good yield or by examination in situ by spectrophotometry or ⁵¹V NMR spectroscopy: V^{II} + XO → V^{IV}O + X; V^{III} + XO → V^VO + X; V^{VO}₂ + V^{III} → 2V^{IV}O; V^{II} + V^{IV}O → V^{III}-O-V^{III}. The last process generates a compound (an intermediate in the first reaction) that has been isolated. V₂OCl₄(py)₆·MeCN crystallizes from acetonitrile/ether in monoclinic space group C2/c with a = 21.093 (9) Å, b = 33.885 (9) Å, c = 12.335 (3) Å, β = 124.33 (2)°, and Z = 8. There are two independent molecules with imposed 2-fold symmetry and essentially linear (178.7 (8)°) and exactly linear V-O-V bridges. Bridge distances are 1.77-1.78 Å, and each V(III) atom is in a distorted octahedral site. Other demonstrated transformations are the electron-transfer reaction V^{II} + V^VO → V^{III} + V^{IV}O and V^{IV}O or V^VO + XO → V^{VO}₂ + X with evolution of chlorine when strong oxo donors (PhIO, m-ClC₆H₄CO₃H) are used. All oxo-transfer and related reactions that interconnect V^{II,III} and the oxovanadium groups V^{IV}O, V^{VO}, V^V₂O₃, V^{IV}V^{VO}₃, and V^{VO}₂ are schematically summarized. This work provides the first systematic examination of the oxo-transfer reactions of V(II-V).

Introduction

In our recent treatment of metal-centered oxygen (oxo) transfer reactions,¹ we have emphasized the functional group aspect of oxometal units, inasmuch as they frequently sustain regiospecific reaction chemistry. The most important oxovanadium groups are **1** and **2**, which have been structurally characterized in a variety



of compounds.^{1,2} Of such species, square-pyramidal [VOX₄]⁻ (X = Cl⁻, Br⁻)^{3,4} and VO(acac)₂⁵ and distorted tetrahedral [VO₂Cl₂]⁻⁶ are among the simplest. Pyramidal group **3** is known only in insoluble metal salts of [V₂O₇]⁴⁻,⁷ and no reaction chemistry of it has been reported. Two remaining groups are derivatives of **2** by protonation or alkylation (**4**, R = H, alkyl) and of **1** and **2** by μ-oxo-bridge formation (**5**). Structurally characterized examples include VO(O-*i*-Pr)(ox)₂⁸ and salts of the anion of

Table I. Absorption Spectral Data for Vanadium(II-V) Complexes in Acetonitrile Solutions

complex	λ _{max} , nm (ε _M)
VCl ₂ (py) ₄	255 (10 600), 411 (1790)
[VCl ₄ (MeCN) ₂] ⁻	327 (3730)
V ₂ OCl ₄ (py) ₆ ^a	252 (16 000), 290 (sh, 4200), 365 (1900), 538 (4100), 674 (sh, 1100)
VOCl ₂ (py) ₂	340 (390), 788 (45)
[VOCl ₄] ²⁻	424 (12), 734 (51)
[VOCl ₄] ⁻	266 (6830), 487 (4770), 650 (180)
[VO ₂ Cl ₂] ⁻	397 (265)

^a Extinction coefficients are approximate values.

VO(OH)(ox)₂^{9,10} (**4**) and V₂O₃(ox)₄¹¹ and [V₂O₃(peida)₂]⁻¹² (**5**). Bridge group **6** contains no terminal oxo ligands and is not a functional group in the sense of **1**, **2**, **4**, and **5**, but, as will be shown, it can be derived from an oxovanadium species. This bridge has been previously demonstrated in two compounds.^{13,14}

The functional group nature of oxovanadium is evident from the early work of Blair et al.,¹⁵ who likened **4** (R = alkyl) to an organic ester and **5** to an anhydride. This concept has since been well developed in the form of a variety of substitution reactions at V^{IV}=O groups¹⁶⁻¹⁸ and by Floriani and co-workers,¹⁰ who

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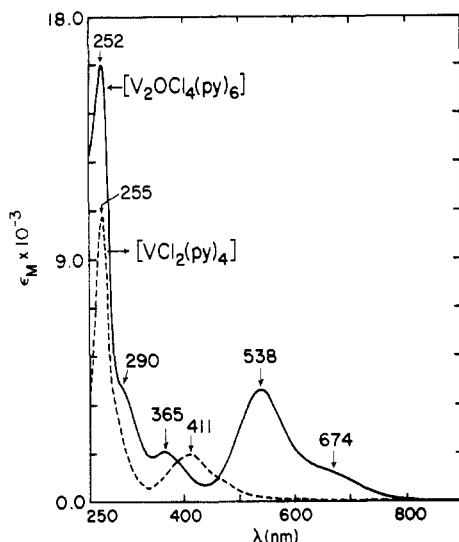
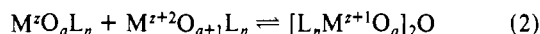
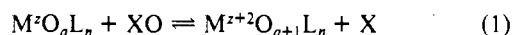


Figure 1. Absorption spectra of $VCl_2(py)_4$ and $V_2OCl_4(py)_6$ in acetonitrile solutions. Absorption maxima are indicated in this and subsequent figures; extinction coefficients of $V_2OCl_4(py)_6$ are approximate.

demonstrated that **4** ($R = H$) supports reactions not unlike that of a carboxylic acid. All of these reactions do not involve a change in oxidation state of the metal. A highly significant reaction type that is capable of forming or removing oxovanadium functional groups is oxo transfer. While there is a multitude of characterized oxovanadium compounds, these have been prepared in a variety of ways and there has been no attempt to develop a rational reaction chemistry based on oxo transfer. Within such a rational framework for any metal, two generalized reactions are to be expected: primary oxo-transfer reaction 1,¹ in which the metal



oxidation state is changed by two units upon reaction with oxo donor/acceptor XO/X ; electron-transfer reaction 2 with μ -oxo-bridge formation. For molybdenum and tungsten, at least, this reaction proceeds unless the rate of reaction 1 is much faster or the reaction is structurally prevented. The oxo-transfer chemistry of vanadium that can be recognized as such is decidedly limited, and nearly all of it has been summarized.¹

We report here the results of the first investigation aimed at demonstrating the transformations that can be achieved by the oxo-transfer reactions of relatively simple V(II–V) complexes. The purpose is to provide a basis of reactivity that defines the scope of the oxo-transfer chemistry of vanadium, with recognition that its application to other vanadium systems may require different reagents XO/X , as the relative stabilities of oxidation states are conditioned by ligand changes.

Experimental Section

Preparation of Compounds. All operations were performed under strictly anaerobic conditions; solvents were purified by standard methods and degassed before use. The compounds $VCl_2(py)_4$,^{19,20} $(R_4N)[VCl_4(MeCN)_2]$,²¹ $VOCl_2(py)_2$ ²² ($py =$ pyridine), $(R_4N)_2[VOCl_4]$,²³ $(R_4N)[VOCl_4]$,²⁴ $(Ph_4P)_2[VO_2Cl_2]$,^{6,25} and iodobenzene²⁶ were pre-

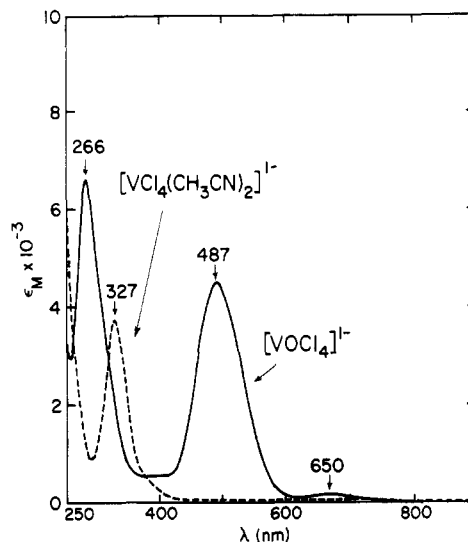


Figure 2. Absorption spectra of $[VCl_4(MeCN)_2]^-$ and $[VOCl_4]^-$ in acetonitrile solutions.

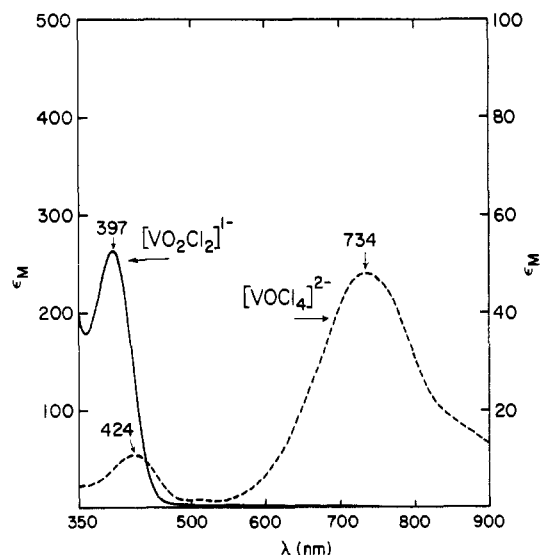


Figure 3. Absorption spectra of $[VOCl_4]^{2-}$ and $[VO_2Cl_2]^-$ in acetonitrile solutions.

pared as previously described. New preparations for certain of these compounds are given below. Vanadium(III) chloride and *m*-chloroperbenzoic acid (MCPBA) were commercial products and were used as received. Absorption spectral data are collected in Table I, and spectra are presented in Figures 1–3. Absorption spectra, and in several cases ⁵¹V NMR spectra, were used to ensure the identity of compounds prepared here by methods that differ from those published.

$V_2OCl_4(py)_6$. (A) $VCl_2(py)_4$ (0.20 g, 0.46 mmol) was dissolved in 35 mL of acetonitrile to give a yellowish brown solution, to which was added 0.05 g (0.23 mmol) of solid PhIO. The solution immediately turned deep purple. After being stirred for 30 min, the solution was reduced in volume to 10 mL. Ether (20 mL) was added, causing the separation of a red-purple amorphous solid. This material was collected by filtration, washed thoroughly with ether, and dried in vacuo overnight to afford 0.11 g ($\approx 67\%$) of an extremely air-sensitive, red-purple solid. A very small quantity of purple, thin, platelike crystals could be obtained after allowing the filtrate to stand overnight at room temperature. The compound was identified by X-ray crystallography as $V_2OCl_4(py)_6 \cdot MeCN$. It is extremely dioxygen- and moisture-sensitive, and thus far it has not been possible to isolate an analytically pure sample.

(B) Equimolar quantities of $VCl_2(py)_4$ (0.175 g, 0.40 mmol) and $VOCl_2(py)_2$ (0.120 g) were dissolved in 30 mL of acetonitrile to form a

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purple solution. Workup proceeded as in method A to give 0.13 g ($\approx 44\%$) of an identical product.

(Et₄N)[VCl₄(MeCN)₂] from (Et₄N)[VOCl₄]. To a solution of 1.00 g (2.95 mmol) of (Et₄N)[VOCl₄] in 25 mL of acetonitrile was added 0.78 g (3.00 mmol) of solid Ph₃P. The solution soon changed in color to pale pink and then to pale yellow, and a copious quantity of light yellow solid separated from solution. The mixture was stirred for 2 h, and 50 mL of ether was added. The solid was filtered off, washed thoroughly with ether, and dried in vacuo overnight to give 1.10 g (92%) of light yellow product. The washings and the filtrate were combined and evaporated to dryness. The pale green residue was dissolved in 10 mL of ether, and this solution was washed several times with water until the organic layer was colorless. Evaporation of the ether gave 0.70 g of a white solid, identified as Ph₃PO (84%) by ³¹P NMR spectroscopy. In another reaction using excess Ph₃P and monitored by ³¹P NMR spectroscopy, it was found that Ph₃PO was formed in situ in 98% yield. The compound prepared here is identical with that obtained from (Et₄N)Cl and VCl₃ in acetonitrile.²¹

(Ph₄P)₂[VOCl₄] from [VCl₄(MeCN)₂]⁻ and [VO₂Cl₂]⁻. To a stirred solution of 0.25 g (0.65 mmol) of Ph₄Pf₆ and 0.16 g (0.32 mmol) of (Ph₄P)[VO₂Cl₂] in 30 mL of acetonitrile was added 0.20 g (0.32 mmol) of solid (Ph₄P)[VCl₄(MeCN)₂]. The solid quickly dissolved and the solution turned bright green. After being stirred for 4 h, the solution was reduced in volume to 5 mL, and 30 mL of ether was added. The material that separated was collected, washed with ether, and dried in vacuo overnight to give 0.53 g (88%) of product as a green microcrystalline solid. The anion of this product is identical with that obtained by the reaction of VOCl₂ with chloride salts in chloroform.²³

(Et₄N)₂[VOCl₄] from VCl₂(py)₄, VCl₂(py)₄ (0.22 g, 0.50 mmol) and (Et₄N)Cl (0.17 g, 1.00 mmol) were dissolved in 30 mL of acetonitrile. To this stirred solution was added 0.11 g (0.50 mmol) of solid PhIO. The initial orange-brown solution immediately became deep purple and then more slowly changed to pale green. After the solution was stirred for 2 h, its volume was reduced to 5 mL. Addition of 40 mL of ether resulted in the separation of a solid, which was collected, washed thoroughly with ether, and dried in vacuo overnight to afford 0.21 g (89%) of product as a pale green microcrystalline solid. The anion of the product is identical with authentic [VOCl₄]²⁻.²³

(Et₄N)₂[VO₂Cl₂] from (Et₄N)₂[VOCl₄]. To a solution of 0.24 g (0.50 mmol) of (Et₄N)₂[VOCl₄] in 30 mL of acetonitrile was added 0.11 g (0.50 mmol) of PhIO. The pale green solution gradually assumed a yellowish color as all the PhIO dissolved. After the solution was stirred for 3 h, its volume was reduced to ca. 5 mL and 30 mL of ether was added. The precipitate was collected by filtration, washed thoroughly with ether, and dried in vacuo to afford 0.13 g (88%) of product as a light yellow microcrystalline solid. ⁵¹V NMR (CD₃CN): -360 ppm; lit.,²⁷ -365 ppm. The anion of this product is identical with that formed by the reaction of VO₂Cl with chloride salts in dichloromethane.⁶ An analogous reaction was carried out with MCPBA as the oxo donor. Product formation was confirmed spectrophotometrically; the only species detectable by ⁵¹V NMR spectroscopy was [VO₂Cl₂]⁻.

(Me₄N)[VO₂Cl₂] from (Me₄N)[VOCl₄]. To a stirred solution of 0.24 g (0.85 mmol) of (Me₄N)[VOCl₄] in 30 mL of acetonitrile was added 0.19 g (0.86 mmol) of PhIO. The latter compound quickly dissolved, and the solution color changed from orange-brown to bright yellow. After the solution was stirred for 2 h, its volume was reduced to 3 mL and 30 mL of ether was added to cause separation of a solid. This material was collected by filtration, washed extensively with ether, and dried in vacuo overnight. The product (0.18 g, 91%) was obtained as a light yellow microcrystalline solid. The same reaction occurs with MCPBA; when monitored by ⁵¹V NMR spectroscopy, formation of the product anion is quantitative. The anion of the product is identical with authentic [VO₂Cl₂]⁻.⁶

Collection and Reduction of X-ray Data. Red-brown, thin, platelike crystals of V₂OCl₄(py)₆·MeCN were grown by adding ether to an acetonitrile solution of the compound and allowing that solution to stand overnight at room temperature. A usable crystal was sealed in a capillary tube under dinitrogen. Crystals of high diffraction quality were not obtained, despite a number of attempts to prepare better crystals. Data collection was performed at ambient temperature on a Nicolet P3F automated four-circle diffractometer equipped with a Mo X-ray source and a graphite monochromator. The orientation matrix and unit cell parameters were derived from a least-squares fit of 25 machine-centered reflections with 2θ values between 10 and 25°. No significant decay of three check reflections measured every 123 reflections was observed during the data collection period. Intensities were corrected for the Lorentz and polarization effects. Data reduction was performed with the

Table II. Crystallographic Data for V₂OCl₄(py)₆·MeCN^a

formula	C ₃₂ H ₃₃ Cl ₄ N ₇ O _V ₂	Z	8
fw	775.36	space group	C2/c
a, Å	21.093 (9)	<i>d</i> _{calc} , g/cm ³	1.42 ^b
b, Å	33.885 (9)	<i>μ</i> , cm ⁻¹	8.74
c, Å	12.335 (3)	<i>R</i> (<i>F</i> _o ²), %	6.55
β, deg	124.33 (2)	<i>R</i> _w (<i>F</i> _o ²), %	6.05
<i>V</i> , Å ³	7280.6 (3.9)		

^a *T* = 297 K, *λ* = 0.71069 Å (Mo Kα). ^b *d*_{obs} not measured because of desolvation of crystal.

program XTape of the SHELXTL structure determination program package (Nicolet XRD Corp., Madison, WI 53711). Monoclinic space group C2/c was derived from the systematic absences *hkl* (*h* + *k* ≠ 2*n*), *h0l* (*h*, *l* ≠ 2*n*), and *0k0* (*k* ≠ 2*n*) and intensity statistics. The space group was confirmed by successful solution and refinement of the structure.

Structure Solution and Refinement. Vanadium atoms were found by direct methods (MULTAN) using the phase set with the highest figure of merit. Subsequent alternating least-squares refinement and difference Fourier maps revealed all other non-hydrogen atoms. The structure was refined by the blocked-cascade least-squares method. Atom scattering factors were taken from a standard source.²⁸ The asymmetric unit consists of two crystallographically independent half-molecules. Both molecules reside on 2-fold axes, with the N–V–O–V–N atom set of one molecule contained by its axis and this set of atoms of the other molecule normal to and bisected by its axis. Isotropic refinement converged at *R* = 15%. Further inspection of the Fourier difference map revealed that one of the pyridine rings on the 2-fold axis was disordered and an acetonitrile solvate molecule was present at a general position. All atoms except the disordered carbon atoms were anisotropically refined. In the last cycle of refinement, no parameter shifted by 0.02 of its esd value. After final refinement, the difference Fourier map showed two random peaks with heights <0.4 e/Å³. Final *R* factors are contained in Table II; positional parameters are listed in Table III.²⁹

Other Physical Measurements. All measurements were made under anaerobic conditions. NMR spectra were acquired on a Brücker WM 300 spectrometer operating at 78.91 MHz for ⁵¹V (neat VOCl₃) and 121.54 MHz for ³¹P (85% H₃PO₄); external standards are indicated. Absorption spectra were recorded on a Perkin-Elmer Lambda-4C spectrophotometer.

Results

For the purpose of investigating the scope of oxo-transfer reactions of V(II–V), we have selected the following set of complexes: VCl₂(py)₄, [VCl₄(MeCN)₂]⁻, VOCl₂(py)₂, [VOCl₄]²⁻, [VOCl₄]⁻, and [VO₂Cl₂]⁻. This set was chosen because its members should reflect the inherent reactivity of a given oxidation state in a somewhat conserved ligand environment, without undue ligand effects on reactivity. Further, their structures are simple and for the most part are known. The structure of VCl₂(py)₄ is trans-octahedral.³⁰ As noted at the outset, [VOCl₄]⁻ is square pyramidal³ and [VO₂Cl₂]⁻ is distorted tetrahedral.⁶ On the basis of the structure of [VOBr₄]²⁻,³ [VOCl₄]²⁻ is expected to be square pyramidal. The d–d absorption spectrum of [VCl₄(MeCN)₂]⁻ in acetonitrile is consistent with an octahedral stereochemistry;^{21a} the detailed structure has not been established.

The reactions considered in the following sections, all of which were conducted in acetonitrile solutions at ambient temperature unless noted otherwise, are summarized in Figure 4. Because of the sparing solubility of PhIO and salts of [VCl₄(MeCN)₂]⁻ in acetonitrile, reaction systems containing these compounds were heterogeneous. Reaction products were identified in situ or after isolation by the characteristic UV/visible spectra in Figures 1–3 or by ⁵¹V NMR spectroscopy.²⁷ The absorption spectra include the more intense features and omit the weaker d–d bands of VCl₂(py)₄ and [VCl₄(MeCN)₂]⁻, which have been reported elsewhere.^{21a,31} The stated yields refer to isolated quantities of pure products. Reactions examined in situ were carried out with

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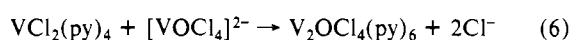
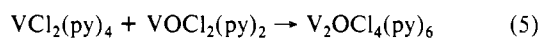
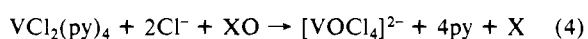
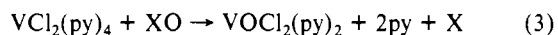
Table III. Positional Parameters for $V_2OCl_4(py)_6 \cdot CH_3CN$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
V(1)	10000 ^a	1129.8 (9)	2500 ^a
V(2)	10000 ^a	2175.9 (9)	2500 ^a
Cl(1)	9925 (2)	1073 (1)	471 (3)
Cl(2)	10768 (2)	2213 (1)	4862 (3)
O(1)	10000 ^a	1656 (3)	2500 ^a
N(1)	10000 ^a	451 (5)	2500 ^a
N(2)	8753 (6)	1111 (3)	1401 (10)
N(3)	10000 ^a	2858 (4)	2500 ^a
N(4)	8956 (5)	2216 (3)	2465 (9)
C(11)	9591 (14)	270 (8)	1385 (24)
C(12)	9724 (18)	-160 (9)	1135 (29)
C(13)	10317 (21)	-355 (10)	2368 (40)
C(21)	8365 (8)	1357 (4)	336 (14)
C(22)	7557 (10)	1399 (5)	-357 (16)
C(23)	7183 (8)	1203 (5)	136 (17)
C(24)	7598 (10)	949 (5)	1226 (17)
C(25)	8391 (9)	913 (4)	1837 (15)
C(31)	10058 (8)	3056 (4)	3505 (14)
C(32)	10049 (8)	3467 (4)	3544 (14)
C(33)	10000 ^a	3683 (6)	2500 ^a
C(41)	8807 (7)	1922 (4)	3048 (12)
C(42)	8095 (8)	1891 (5)	2885 (13)
C(43)	7540 (8)	2185 (5)	2125 (13)
C(44)	7704 (8)	2494 (5)	1592 (15)
C(45)	8435 (8)	2501 (4)	1756 (13)
V(3)	6012 (1)	1165.8 (6)	3607 (2)
Cl(3)	6004 (2)	1008 (1)	5502 (3)
Cl(4)	6268 (2)	1314 (1)	1987 (3)
O(2)	5000 ^a	1161 (3)	2500 ^a
N(5)	7321 (6)	1213 (3)	5083 (11)
N(6)	6118 (6)	543 (3)	3344 (12)
N(7)	6025 (6)	1801 (3)	3946 (9)
C(51)	7799 (8)	1067 (4)	4800 (14)
C(52)	8608 (9)	1129 (6)	5661 (19)
C(53)	8878 (10)	1340 (6)	6799 (20)
C(54)	8385 (10)	1486 (5)	7123 (17)
C(55)	7582 (9)	1427 (4)	6211 (15)
C(61)	5775 (9)	390 (5)	2136 (16)
C(62)	5819 (11)	-3 (6)	1884 (18)
C(63)	6195 (13)	-262 (5)	2923 (24)
C(64)	6610 (12)	-118 (5)	4200 (20)
C(65)	6536 (10)	284 (5)	4354 (16)
C(71)	6494 (8)	2045 (5)	3873 (13)
C(72)	6431 (9)	2457 (5)	3964 (15)
C(73)	5898 (10)	2613 (5)	4101 (15)
C(74)	5422 (9)	2354 (5)	4236 (13)
C(75)	5488 (8)	1940 (4)	4133 (12)
N(10)	12031 (16)	161 (10)	1805 (30)
C(100)	11948 (28)	-173 (13)	1866 (47)
C(101)	11973 (22)	-573 (7)	1961 (35)

^aOn special position.

ca. 5–10 mM vanadium reactants. Very few reactivity properties of any member of the set have been previously reported.^{24,27,32}

Oxo Transfer to V(II). (A) **Reactions.** The V(II) reactant is $VCl_2(py)_4$, which possesses a band of moderate intensity at 411 nm (Figure 1). Reactions 3 and 4 with $XO = PhIO$ proceed in



two stages. Upon the addition of the oxo donor, the initial yellow-brown solution immediately turns deep purple and then more slowly to the pale green color of $VOCl_2(py)_2$ ($\lambda_{max} = 340, 788$ nm). Similar observations were made for reaction 4, which afforded green $[VOCl_4]^{2-}$, with d-d bands at 424 and 734 nm (Figure 3), in high yield (89%). The purple intermediate was isolated as a red-purple solid from the reaction of $VCl_2(py)_4$ with

VANADIUM-MEDIATED OXO TRANSFER REACTIONS

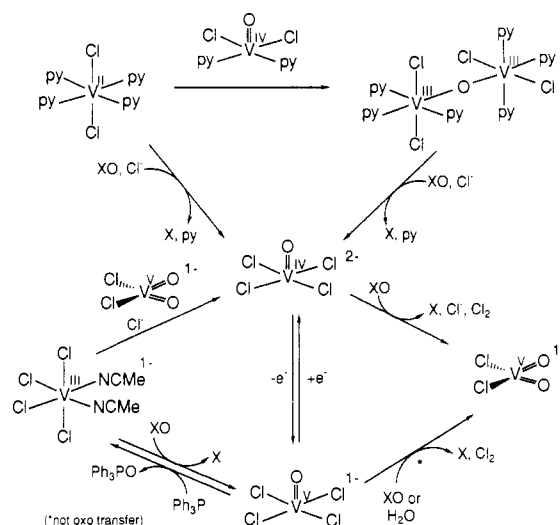


Figure 4. Schematic representation of oxo-transfer and other reactions of V(II–V) examined in this work.

0.5 equiv of $PhIO$ and from reaction 5 and was identified as $V_2OCl_4(py)_6$. This compound is readily recognized by a prominent visible band at 538 nm and a shoulder at 674 nm (Figure 1). Electron-transfer reactions 5 and 6 are fast compared with primary oxo-transfer reactions 3 and 4. The result is that the only vanadium product present in any appreciable concentration after 0.5 equiv of the oxo donor is consumed is the binuclear species. Because of the slow degradation of $V_2OCl_4(py)_6$ in acetonitrile, it was difficult to establish whether or not reaction 5 is reversible.

In Me_2SO solvent, the formation of the intermediate in reactions 3 and 4 is nearly instantaneous. In this medium, the intermediate has a red-brown color, with $\lambda_{max} = 489$ and 575 (sh) nm. Its disappearance was slow, taking hours at 60 °C. The final spectra were those of Me_2SO solutions prepared from $VOCl_2(py)_2$ or $[VOCl_4]^{2-}$.

The system with the 1:13:2 $VCl_2(py)_4:Ph_3PO:Et_4NCl$ composition at 60 °C for 18 h showed no oxidation of V(II). The 1:10:2 $VCl_2(py)_4:Ph_3AsO:Et_4NCl$ system under the same conditions underwent a color change from red-orange to yellow, but the absorbance increase in the visible region of $V^{IV}=O$ chromophores was too small to indicate appreciable reaction.

(B) Structure of $V_2OCl_4(py)_6$. This compound as its acetonitrile monosolvate was isolated in a crystalline form that contained two inequivalent molecules with imposed C_2 axes. Structures are shown in Figure 5, and metric parameters are listed in Table IV. In molecule 1, the C_2 axis contains the atom set V(1,2), O(1), and N(1,3) whereas in molecule 2 this axis is perpendicular to the V(3)–O(2)–V(3') unit. The two molecules are perpendicular to each other in the asymmetric unit. Molecule 1 includes one pyridine ligand, which is somewhat disordered. Both molecules have almost identical geometries and metric values, so that the following discussion applies to both.

The compound is a linear oxo-bridged $[VOV]^{4+}$ dimer, containing the group 6, with the V(III) atoms in a distorted octahedral environment. The V–O distances of 1.77 (1)–1.78 (1) Å are indicative of some multiple bonding, which is also reflected in a trans influence on the bond lengths V–N(1,3,5). These are 0.12–0.13 Å longer than the V–N bonds cis to the V–O–V bridge. Octahedral single-bond V(III)–O distances involving anionic ligands are 1.9–2.0 Å.³³ The V–Cl distances of 2.396 (4)–2.424 (4) Å are significantly longer (0.07–0.12 Å) than those in $mer-VCl_3(THF)_3$ ³⁴ but are within 0.02–0.04 Å of the bond lengths in

(33) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(34) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $V_2OCl_4(py)_6 \cdot MeCN$

Molecule 1			
V(1)-O(1)	1.78 (1)	V(2)-O(1)	1.77 (1)
V(1)-Cl(1)	2.424 (4)	V(2)-Cl(2)	2.411 (3)
V(1)-N(1)	2.30 (2)	V(2)-N(3)	2.31 (2)
V(1)-N(2)	2.18 (1)	V(2)-N(4)	2.18 (1)
V(1)-O(1)-V(2)	180		
Cl(1)-V(1)-Cl(1')	170.8 (3)	Cl(2)-V(2)-Cl(2')	174.1 (2)
N(2)-V(1)-N(2')	176.5 (6)	N(4)-V(2)-N(4')	172.9 (6)
O(1)-V(1)-Cl(1)	94.6 (1)	O(1)-V(2)-Cl(2)	92.9 (1)
O(1)-V(1)-N(2)	91.8 (3)	O(1)-V(2)-N(4)	93.5 (3)
Cl(1)-V(1)-N(2)	90.2 (3)	Cl(2)-V(2)-N(4)	90.2 (3)
Cl(1')-V(1)-N(2)	89.5 (3)	Cl(2')-V(2)-N(4)	89.4 (3)
Cl(1)-V(1)-N(1)	85.4 (1)	Cl(2)-V(2)-N(3)	87.1 (1)
N(2)-V(1)-N(1)	88.2 (3)	N(4)-V(2)-N(3)	86.5 (3)
Cl(1)-V(1)-O(1)-V(2)-Cl(2)	30.7		
ring 2/ring 4 ^a	19.2	ring 3/ring 4	107.8
Molecule 2			
V(3)-O(2)	1.770 (2)	V(3)-Cl(3)	2.404 (4)
V(3)-Cl(4)	2.396 (4)	V(3)-N(5)	2.30 (1)
V(3)-N(6)	2.17 (1)	V(3)-N(7)	2.18 (1)
V(3)-O(2)-V(3')	178.7 (8)	Cl(3)-V(3)-Cl(4)	169.6 (2)
N(5)-V(3)-O(2)	176.3 (5)	N(6)-V(3)-N(7)	174.3 (5)
O(2)-V(3)-Cl(3)	94.6 (2)	O(2)-V(3)-Cl(4)	95.8 (1)
O(2)-V(3)-N(6)	93.1 (5)	O(2)-V(3)-N(7)	92.3 (5)
Cl(3)-V(3)-N(5)	84.8 (3)	Cl(4)-V(3)-N(5)	84.9 (3)
Cl(3)-V(3)-N(6)	89.2 (3)	Cl(4)-V(3)-N(6)	89.4 (3)
Cl(3)-V(3)-N(7)	92.3 (3)	Cl(4)-V(3)-N(7)	88.1 (3)
N(5)-V(3)-N(7)	84.1 (4)	N(5)-V(3)-N(6)	90.5 (5)
Cl(4)-V(3)-O(2)-V(3')-Cl(3')	25.0		
Cl(4)-V(3)-O(2)-V(3')-Cl(4')	25.3		
Cl(3)-V(3)-O(2)-V(3')-Cl(3')	25.8		
Cl(3)-V(3)-O(2)-V(3')-Cl(4')	25.0		
ring 5/ring 6	68.2	ring 5/ring 7	61.2
ring 6/ring 6'	159.9	ring 7/ring 7'	5.0

^aRings numbered by nitrogen atom number.

$V_2OCl_4(THF)_6$.¹³ The halves of the molecule depart from an eclipsed conformation of chlorine atoms by Cl-V-O-V-Cl torsional angles of 25–31°. Repulsions of ligands across the oxo bridge are indicated by trans Cl-V-Cl and N-V-N angles of 170–174 and 173–177°, respectively. The ligand displacements associated with these angles could contribute to the longer V-N bonds trans to the bridging oxo ligand.

$V_2OCl_4(py)_6$ is structurally similar to $V_2OCl_4(THF)_6$,¹³ with the main difference being the Cl-V-O-V-Cl torsional angle in the latter, which is 81.3°. Consequently, the chloride and THF ligands on one vanadium atom are staggered with respect to those on the other atom. In this aspect, $V_2OCl_4(py)_6$ is more nearly eclipsed. $V_2OCl_4(THF)_6$ is also a purple chromophore, with $\lambda_{max} = 487$ nm for the presumably analogous charge-transfer band in acetonitrile.¹³ The only other structurally characterized [VOV]⁴⁺ complex, $V_2O(SCH_2CH_2NMe_2)_4$,^{14,35} has a linear bridge and five-coordinate vanadium and displays an intense band at 463 nm in acetonitrile.

Oxo Transfer to V(III). The V(III) source is $[VCl_4(MeCN)_2]^-$, which exhibits a strong band at 327 nm and no appreciable absorption in the visible region (Figure 2). Primary oxo-transfer reaction 7 with a stoichiometric quantity of oxo donor proceeds readily to afford the indicated V(V) product. However, in all cases $[VO_2Cl_2]^-$ is formed as well. Both complexes were detected by ⁵¹V NMR spectroscopy. Because of the heterogeneous nature of

(35) After this paper was submitted for publication, there appeared a brief report of the compound $V_2OCl_4(py)_6$, prepared by a method different from reactions 5 and 6: Christou, G.; Heinrich, D.; Money, J. K.; Rambo, J. R.; Huffman, J. C.; Folting, K. *Polyhedron* 1989, 8, 1723.

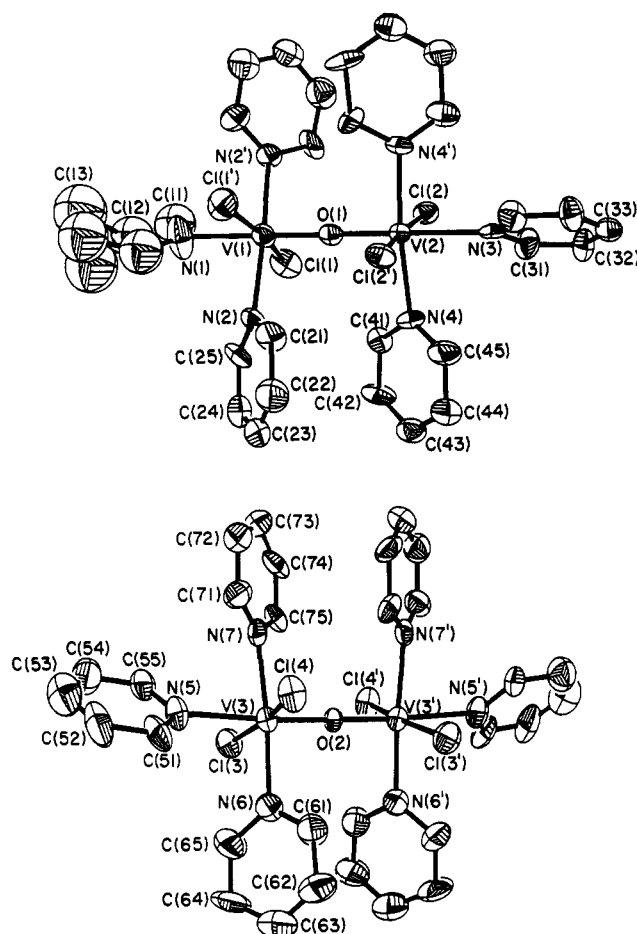
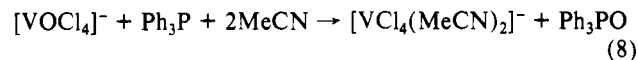


Figure 5. Structure of $V_2OCl_4(py)_6$ as its acetonitrile solvate, showing 50% probability ellipsoids and the atom-labeling scheme: (top) molecule 1, with atoms N(1,3), V(1,2), and O(1) on the C_2 axis; (bottom) molecule 2, with the C_2 axis perpendicular to the V(3)-O(2)-V(3') unit and containing O(2). Primed and unprimed atoms are related by a C_2 axis.

the reaction system, the ratio of the two products was sensitive to experimental conditions such as particle size, solution volume, and stirring rate. However, $[VOCl_4]^-$ was always the main product when 1 equiv of PhIO was employed. When 2 equiv of this oxo donor is used, the only product is $[VO_2Cl_2]^-$. The means of formation of this complex is described below.

When a ca. 10 mM solution of $[VCl_4(MeCN)_2]^-$ in Me_2SO was heated at 60 °C for 3 days, the final spectrum was identical with that of $[VOCl_4]^{2-}$ in Me_2SO .³⁶ In a separate solution, it was established that $[VOCl_4]^-$ is rapidly reduced in Me_2SO , affording this same spectrum. From these results we conclude that oxo transfer to V(III) has occurred but that the product, $[VOCl_4]^-$, is unstable in the solvent medium.

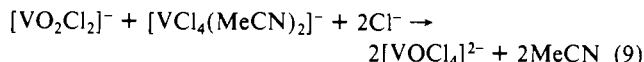
Oxo Transfer from V(V). The V(V) source is $[VOCl_4]^-$, whose absorption spectrum contains an intense visible band at 487 nm (Figure 2). Reaction 8 proceeds rapidly and nearly quantitatively



to afford the V(III) product as its sparingly soluble $(Me_3NCH_2Ph)^+$ salt (92%). The phosphine oxide was isolated in 84% yield. In an in situ reaction with excess Ph_3P and with monitoring by ³¹P NMR spectroscopy, Ph_3PO was formed quantitatively.

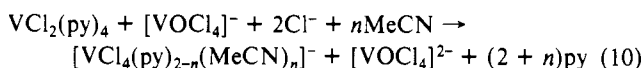
Intermetal V(III,V) Oxo Transfer. The complex $[VO_2Cl_2]^-$ is reduced slowly by tertiary phosphines at ambient temperature in a somewhat complicated reaction that has not been fully defined. However, reaction 9 proceeds immediately, affording the V(IV)

(36) The difference between this spectrum (λ_{max} (ϵ_M) 700 (sh, 23), 810 (30)) and that of $[VOCl_4]^{2-}$ in acetonitrile (Figure 3) suggests partial substitution of chloride ligands by solvent.



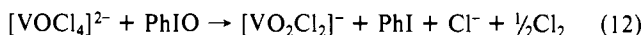
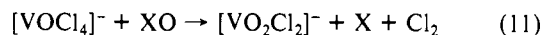
product (88%). This reaction is doubtlessly initiated by the formation of the bridged (presumably solvated) intermediate $[\text{Cl}_2\text{V}(\text{O})-\text{O}-\text{VCl}_4]^{2-}$, which dissociates upon electron transfer.

Electron Transfer. Given the intermediacy of a $[\text{VOV}]^{4+}$ dimeric species from the interaction of V^{II} and $\text{V}^{\text{IV}}=\text{O}$ in reactions 3 and 4 and its isolation in stable form from reactions 3 and 5, we examined the possibility of a stable intermediate formed from V^{II} and $\text{V}^{\text{V}}=\text{O}$. Reaction 10 with excess chloride generated an



instantaneous green color. The in situ spectrophotometric yield of the $\text{V}(\text{IV})$ product was quantitative. The $\text{V}(\text{III})$ product was detected by a sharp band at 320 nm but could not be quantitated accurately owing to band overlap. Under the assumption that the extinction coefficient of the product at 320 nm is the same as that of $[\text{VCl}_4(\text{MeCN})_2]^-$ at 327 nm, its extent of formation was no less than 75% of the reaction stoichiometry. The appearance of this band at 320 nm rather than 327 nm (Figure 2) suggests that pyridine may be bound in the $\text{V}(\text{III})$ product.

Oxide Formation Reactions. Two remaining reactions have been demonstrated, in which the reactants contain $\text{V}(\text{IV})$ and $\text{V}(\text{V})$. These are not capable of sustaining primary oxo-transfer reaction 1. Nonetheless, they are reactive with very strong oxo donors¹ in processes that result in the formation of coordinated oxide ion. Thus, reaction 11 with $\text{X} = \text{PhIO}$ proceeds with evolution of



chlorine³⁷ and nearly quantitative formation (91%) of the $\text{V}(\text{V})$ product. When $\text{X} = \text{MCPBA}$, $[\text{VO}_2\text{Cl}_2]^-$ was the only product detectable in situ by ⁵¹V NMR spectroscopy. Reaction 12 affords the same product in high yield (89%). In these reactions, the oxygen atom transferred from the donor is reduced to oxide by chloride ligand oxidation or by this process and oxidation of $\text{V}(\text{IV})$ to $\text{V}(\text{V})$. It is likely that intermediate $\text{V}(\text{IV})$ and $\text{V}(\text{V})$ peroxides are formed, followed by the reduction of peroxide to oxide.

Discussion

Reactions 3, 4, 7, and 8 are examples of primary oxo-transfer reaction 1. Reactions 5 and 6 are examples of electron-transfer reaction 2 ($a = 0$) in which a μ -oxo bridge is formed. We have also termed such reactions as "incomplete" oxo transfer.¹ Reaction 9 is a special case of intermetal oxo transfer, in which one reactant carries the oxo ligands and the (presumed) unsymmetrical μ -oxo bridge in the intermediate is broken to give identical products. These reactions involve oxovanadium groups 1 and 2.

Thermodynamic Reactivity Scale. In the construction of a systematic body of oxo-transfer chemistry, a predictive thermodynamic scale of reactivities is a most important goal. We have introduced such a scale based on the enthalpy changes for the reaction (couple) $\text{X} + \frac{1}{2}\text{O}_2(\text{g}) = \text{XO}$, where X is any oxygen atom acceptor.^{1,38,39} When couples are arranged in a series of decreasing ΔH values, the resultant tabulation may be used in the manner of a table of standard redox potentials. Thus, under the criterion of exothermicity, the reduced member of a given couple can reduce the oxidized member of another couple with a larger (less negative) ΔH . An extensive reactivity series is given

(37) Chlorine was detected by treatment of an aliquot of the reaction solution with excess Et_4NI followed by titration with standard aqueous $\text{Na}_2\text{S}_2\text{O}_3$ with a starch solution indicator.

(38) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.

(39) For an independent formulation of a reactivity scale, cf.: Tolman, C. A.; Herron, N. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Sawyer, D. T., Martell, A. E., Eds.; Plenum Press: New York, 1988; pp 283-303.

OXO TRANSFER REACTIONS OF VANADIUM

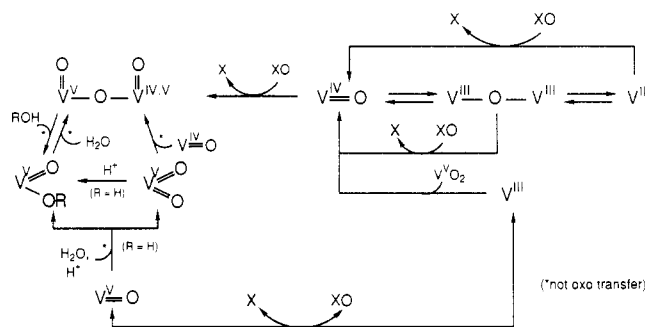


Figure 6. Generalized representation of the oxo-transfer and related reactions that interrelate oxovanadium groups 1, 2, 4, and 5 and oxidation states $\text{V}(\text{II-V})$. Double-headed curved arrows indicate that transformations between species connected with joined straight-line segments are bidirectional; single-headed arrows indicate a unidirectional transformation. Non-oxo-transfer processes are marked (*).

elsewhere.¹ The following series illustrates the problem of placement of certain vanadium couples in the reactivity scale:

	X	XO	ΔH , kcal/mol
a	PhI	PhIO	
b	$\text{Me}_2\text{S}(\text{g})$	$\text{Me}_2\text{SO}(\text{g})$	-27
c	$[\text{VCl}_4(\text{MeCN})_2]^-$	$[\text{VOCl}_4]^- + 2\text{MeCN}$	
d	$\text{VCl}_2(\text{py})_4 + 2\text{Cl}^-$	$[\text{VOCl}_4]^{2-} + 4\text{py}$	
e	$\text{Ph}_3\text{P}(\text{g})$	$\text{Ph}_3\text{PO}(\text{g})$	-67

All couples containing $\text{V}(\text{II,III})$ lie below couple b inasmuch as the reduced forms are oxidized by Me_2SO , which is a weaker oxo donor than PhIO or MCPBA .¹ The placement of couple c comes from the observation that its reduced form in Me_2SO solution yields $[\text{VOCl}_4]^{2-}$ quantitatively. It is assumed that $[\text{VOCl}_4]^-$ was the initial oxo-transfer product. The relative positions of couples c and d could not be directly established by competitive oxo transfer inasmuch as the instantaneous nature of reaction 10 suggests that it involves electron rather than oxo transfer.⁴⁰ The relative placement of couples d and e is uncertain because of the lack of reaction between the $\text{V}(\text{II})$ complex and Ph_3PO , and the failure of Ph_3P to reduce the $\text{V}(\text{IV})$ complex, both under forcing conditions. $\text{VCl}_2(\text{py})_4$ also did not react with Me_2SO_2 ($\text{Me}_2\text{SO}/\text{Me}_2\text{SO}_2$, -52 kcal/mol) and reacted sluggishly if at all with Ph_3AsO ($\text{Ph}_3\text{As}/\text{Ph}_3\text{AsO}$, ca. -35 kcal/mol). Clearly, certain of the reaction systems are under kinetic, not thermodynamic, control.

Summary of Vanadium-Mediated Oxo Transfer. All known oxo-transfer reactions of vanadium involving mono- and binuclear species are schematically summarized in the diagram of Figure 6. The reactions demonstrated in this work and those collected elsewhere¹ form the basis of the scheme. Oxidation states and oxovanadium groups accessible in uni- or bidirectional transformations are connected by straight-line segments. The scheme is generalized; not all transformations are spontaneous with a given vanadium complex or oxo donor/acceptor. It does not include peroxide species or higher nuclearity oxovanadium units formed at least in part by oxo transfer, although the elementary steps in elaborating such units are presumably included in the scheme. The organometallic oxo clusters prepared by Bottomley and co-workers^{1,41} are prominent examples of polynuclear species formed under oxo-transfer conditions. Results supporting the various transformations are briefly summarized.

(A) $\text{V}^{\text{II}} \rightarrow \text{V}^{\text{IV}}=\text{O}$. Reactions 3 and 4 effect the oxidative transformation. This same reaction probably occurs in the reduction of sulfoxides⁴² and *N*-oxides⁴³ and the reductive cleavage

(40) Proof of this statement would require a vanadium isotope labeling experiment.

(41) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

(42) Olah, G. A.; Prakash, G. K.; Ho, T.-L. *Synthesis* **1976**, 810.

(43) Anderson, S.; Constable, E. C.; Seddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2247.

of oximes to imines⁴⁴ by aqueous VCl_2 and in the deoxygenation of epoxides by reactants formulated as bis(β -keto enolato)vanadium(II) complexes.⁴⁵ The vanadium-containing products in these systems were not identified. A $[VOV]^{4+}$ intermediate, as an unstable brown chromophore with $\lambda_{max} = 425$ nm, was first identified by Newton and Baker⁴⁶ in the reaction of V^{2+} and VO^{2+} in aqueous acid solution. This same species intervenes in one pathway for the oxidation of V^{2+} to VO^{2+} by O_2 or H_2O_2 under acid conditions,^{47,48} a matter recently proven by a pulse-radiolysis study.⁴⁸ As we have observed earlier,¹ the formation of V^{3+} from the reaction of V^{2+} with N -oxides in aqueous solution⁴⁶ probably proceeds at least in part by primary oxo transfer to form VO^{2+} followed by generation of the $[VOV]^{4+}$ intermediate and its cleavage under acid conditions to V^{3+} .

The reverse transformation $V^{IV}=\text{O} \rightarrow V^{II}$ has not yet been effected. On the basis of the thermodynamic reactivity scale in aqueous solution,¹ the V^{2+} ion ranks as one of the stronger oxo acceptors in water. $[VOCl_4]^{2-}$ was not reduced by an excess (5–10 equiv) of Ph_3P at 60–70 °C for at least 2 h in acetonitrile solution.

(B) $V^{III} \rightleftharpoons V^V=\text{O}$. Reaction 7 is the only example of the oxidative transformation in which the $V(V)$ product has been isolated. Reaction 8 affords the reductive transformation. Earlier, Nicholls and Wilkinson²⁴ claimed the reduction of $[VOCl_4]^-$ by Ph_3P in nitromethane to give $[VCl_6]^{3-}$ as the major product. No proof was presented for its formation. All oxo-transfer reactions of the $V^V=\text{O}$ group, which is commonly found only in VOL_3 compounds ($L = \text{halide}, NO_3^-$), have been carried out with $[VOCl_4]^-$. A more extensive chemistry of this group in other ligand settings should be possible, as indicated by the recent isolation and structure determination of a new $V^V=\text{O}$ complex⁵⁰ and the generation of other species containing this group in solution.⁵¹

(C) $V^{IV}=\text{O} \rightarrow V^V_2O_3$. This transformation is included on the basis of the formation of the $V^V_2O_3$ group 5 by aerial oxidation of $V^{IV}=\text{O}$ complexes, one example being the preparation of $V_2O_3(\text{ox})_4$.¹⁰ This is a likely reaction with other oxo donors.

(D) **Non-Oxo-Transfer Reactions.** Certain of these are included in order to demonstrate conversion reactions of groups 1, 2, 4, and 5. Group 5 can also be produced by the hydrolysis of $V^V=\text{O}$,²⁷ which presumably yields $V^VO(OH)$ or V^VO_2 initially, and also by hydrolysis of the $V^VO(OR)$ group 4.¹⁵ The mixed-valence form of 5 is usually prepared by reaction of the $V^{IV}=\text{O}$ and V^VO_2 groups.⁵² Reaction 11 and 12 are new routes to the V^VO_2 group, albeit with oxidative sacrifice of ligands.

Evolution of the reaction scheme of Figure 6, which conveys the known oxo-transfer and related reactions of $V(II-V)$ and hence reactions that are conceivable in new systems, is the first step in formulating the systematic oxo-transfer chemistry of the element. The second step is the placement of representative vanadium complexes in the thermodynamic reactivity scale. In that respect, the uncertain situation presented above underscores once again the need for calorimetric determination of the enthalpies of oxo-transfer reactions.

Related schemes for the oxo and imido group transfer reactions of molybdenum are given elsewhere.⁵³

Acknowledgment. This research was supported by NSF Grant CHE 85-21365. X-ray equipment was obtained through NIH Grant 1 S10 RR-2247.

Supplementary Material Available: Tables of crystallographic data for $V_2OCl_4(\text{py})_6$, including details of data collection and tabulations of thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions (9 pages); a listing of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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