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Reduction of Nitrate by Diammonium Oxopentachloromolybdate(V) in Dimethylformamide

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The reduction of nitrate by diammonium oxopentachloromolybdate(V) ($(NH_4)_2MoOCl_5$) in anhydrous dimethylformamide (DMF) has been investigated as a model for biological nitrate reduction. The stiochiometric reaction is $MoOCl_5^{2-} + NO_3^- \rightarrow MoO_2Cl_2 + NO_2 + 3Cl^-$. The reaction is first order in total Mo(V) and NO_3^- and is inhibited by Cl^-. A mechanism involving the formation of an intermediate complex, $MoOCl_3NO_3^-$, followed by an intramolecular electron transfer to form products has been developed to explain the kinetic results. A rate constant of $(1.62 \pm 0.15) \times 10^{-4}$ sec^{-1} for the overall reaction has been obtained and activation parameters of 18.3 ± 0.4 kcal mol^{-1} for $\Delta H^{\ddagger}$ and -14 ± 3 cal mol^{-1} K^{-1} at 25° for $\Delta S^{\ddagger}$ determined. The implications for enzymatic nitrate reduction are discussed.

The major source of nitrogen for most plants and microorganisms is nitrate, which is reduced in a number of steps by the organisms to ammonia. The first stage in this process, the reduction of nitrate to nitrite, is catalyzed by a group of enzymes, the nitrate reductases, all of which require molybdenum as a cofactor.[1] In addition to molybdenum, flavine,[2] *b*-type cytochromes,[2] and nonheme iron cofactors[3,4] may also be required, depending on the specific enzyme.

Little is known concerning the binding site of molybdenum, its oxidation states, or its function in the catalytic processes of the nitrate reductases. Early work suggested the metal shuttles between the +5 and +6 oxidation states, transferring electrons from a reduced flavine cofactor to nitrate.[5] More recently, electron spin resonance (ESR) studies of the enzymes from *M. denitrificans*[3] and *E. coli*[4] have shown the presence of Mo(V) during the catalytic cycle. Evidence from both enzymatic and model investigations suggests the protein at the molybdenum binding site provides a nonaqueous environment similar to an aprotic medium.[1,6,7]

Previous attempts to reduce nitrate by molybdenum(V) species in aqueous solution have produced mainly nitric oxide,[8,9] due to the more rapid reduction of nitrite than nitrate by Mo(V) in water.[8,10] A recent preliminary report indicates NO_2 is formed upon reduction of nitrate by molybdenum(V) complexes in dichloromethane solution.[11]

If the environment at the molybdenum binding site is indeed nonaqueous, an aprotic solvent of moderate dielectric constant should provide a more appropriate environment than water for model studies of nitrate reduction. As part of a program of model studies for molybdenum enzymes, the reduction of nitrate by diammonium oxopentachloromolybdate(V), $(NH_4)_2MoOCl_5$, in anhydrous dimethylformamide (DMF) is reported here.

Experimental Section

Materials. Spectrograde DMF was obtained from Aldrich Chemical Co. It was distilled in vacuo over P_2O_5 (2.5–8.0 Torr, 33–49°) and stored over Linde molecular sieves, Type AW-500, for at least 48 hr before use. This technique is reported to reduce the H_2O content to <18 ppm.[12]

$(NH_4)_2MoOCl_5$ was prepared and purified as described.[13] Tetraethylammonium nitrate (Et_4NNO_3) and $NaNO_3$, Eastman Kodak and Mallinckrodt products, respectively, were dried in vacuo over P_2O_5 before use. MoO_2Cl_2 was obtained from Alfa Products and used without further purification. NO_2 and N_2 (99.99%) were obtained from Matheson. $NH_4MoOCl_4 \cdot CH_3CN$ was synthesized according to the method of Horner and Tyree.[14]

Methods. Stock solutions of $(NH_4)_2MoOCl_5$ and Et_4NNO_3 or $NaNO_3$ were prepared in deaerated DMF and kept under a stream of N_2 in a constant-temperature bath. The reaction was initiated by mixing the proper amounts of stock solutions, using gas-tight syringes, under N_2 in a cuvette equipped with a rubber septum. The cuvette was kept in a thermostated cell holder in a Varian 635 spectrometer and the absorbance of $(NH_4)_2MoOCl_5$ at 315 nm as a function of time was recorded on a Hewlett-Packard X-Y recorder. The method was standardized by preparing known solutions of $(NH_4)_2MoOCl_5$ in DMF and measuring their absorbance at 315 nm. Over the concentration range used (10^{-5}–10^{-4} *M*) Beer's law is obeyed (ϵ 5.36 × 10^3). Absorbance by NO_3^- is negligible at 315 nm while small corrections for the absorbance of NO_2 and MoO_2Cl_2 were necessary ($\epsilon_{NO_2} + \epsilon_{MoO_2Cl_2} = 633$) at the concentrations used or expected to be formed in the reaction. The molar absorptivity (5.23 × 10^3) at 315 nm of solutions of $(NH_4)_2MoOCl_5$ in DMF was unaffected by added Et_4NCl concentrations up to 2.5 × 10^{-2} *M*.

Except in cases where NO_2 was to be detected or HNO_2 measured, N_2 was continuously passed over the solution in the cuvette during the reaction. For HNO_2 analysis, samples were withdrawn with a small gas-tight syringe and added to an aqueous acidic solution for HNO_2 determination by the method of Shinn.[15] Under these conditions, the NO_2 rapidly disproportionates to NO_3^- and HNO_2.[8,16] Product identification was accomplished by preparing solutions of MoO_2Cl_2 and NO_2 and comparing their absorption spectra with the spectrum of the reaction mixture.

In all cases, extreme care was necessary to prevent the absorption of H_2O and O_2 by the solutions, since these react with $(NH_4)_2MoOCl_5$, giving unreproducible results.

All kinetic data were treated with appropriate programs on a PDP-8 computer to give rate constants and activation parameters.

Results

Stoichiometry. When nitrate (tetraethylammonium nitrate, Et_4NNO_3, or $NaNO_3$) is added to a solution of $(NH_4)_2MoOCl_5$ in DMF, the characteristic spectrum of $(NH_4)_2MoOCl_5$ changes with time to that of a solution of MoO_2Cl_2 and NO_2. Samples, withdrawn from the reaction, were tested for nitrite in acidic aqueous solution, while the amount of $(NH_4)_2MoOCl_5$ reacted was determined from spectrophotometric analysis of the original solution. The ratio of $(NH_4)_2MoOCl_5$ reacted to HNO_2 formed was found to be 2.2 ± 0.2. Furthermore, when the rate of the reaction was determined by following HNO_2 production or $(NH_4)_2MoOCl_5$ disappearance, the results were essentially identical (see below). Thus, the stoichiometry as determined by analysis in acidic aqueous solution is

$$2MoOCl_5^{2-} + NO_3^- + 5H_2O \rightarrow HNO_2 + 2H_2MoO_4 + 10Cl^- + 5H^+$$

(Mo(VI) is indicated as H_2MoO_4; in acidic solution, however, it is polymerized to some extent.)

The HNO_2 arises by the well-known disproportionation of NO_2 in H_2O[8,16]

$$H_2O + 2NO_2 \text{ (or } N_2O_4) \rightleftarrows NO_3^- + HNO_2 + H^+$$

This was verified by bubbling NO_2 through DMF and testing the solution for HNO_2 in the same manner.

The stoichiometric equation in DMF may therefore be written

$$\mathrm{MoOCl_5}^{2-} + \mathrm{NO_3}^- \rightarrow \mathrm{MoO_2Cl_2} + \mathrm{NO_2} + 3\mathrm{Cl}^-$$

Kinetics. The rate of the reaction was determined by measuring the $(NH_4)_2MoOCl_5$ concentration or the HNO_2 produced with time. The rates obtained were identical within experimental error.

The rate of the reaction was found to be dependent on both NO_3^- and $(NH_4)_2MoOCl_5$ concentrations. Pseudo-first-order plots (excess NO_3^-, first order in $(NH_4)_2MoOCl_5$) were linear to approximately 50% reaction, deviating in a negative direction beyond this. Since negative deviations in kinetic plots are often indicative of product inhibition, additional chloride (Et_4NCl) was added to the reaction, resulting in a decreased rate, while addition of MoO_2Cl_2 or NO_2 had no effect on the rate. Furthermore, as the additional chloride ion concentration was increased, the linearity of the plots increased beyond 50% and good pseudo-first-order plots were obtained when excess Et_4NCl ($>10^{-2}$ *M*) was added.

Second-order rate constants, evaluated from the linear portion of the plots, gave consistent values when Et_4NNO_3 was used as the source of nitrate but gave values that decreased with increasing nitrate concentration when $NaNO_3$ was used. This appears to be due to ion-pair formation between Na^+ and NO_3^- in DMF, for which the ion-pair formation constant is reported to be[17]

$$\frac{[\mathrm{Na^+NO_3^-}]}{[\mathrm{Na^+}][\mathrm{NO_3^-}]} = K_\mathrm{p} = 43$$

When $[NO_3^-]$ calculated from this equilibrium is used in the rate expression, the rate constants are consistent and in good agreement with the rate constants for the results with Et_4NNO_3. Apparently, Et_4NNO_3 does not form ion pairs in DMF at the concentrations used. A search of the literature failed to find any data indicating pair formation for this compound.

Discussion

The best fit for the experimental data in the absence of added Cl^- was obtained by assuming an initial Cl^- concentration equivalent to the initial $(NH_4)_2MoOCl_5$ concentration. With this assumption, a rate expression was obtained (see below) that gives linear plots to >90% reaction.

The results are consistent with the mechanism of eq 1–3.

$$\mathrm{MoOCl_5}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MoOCl_4}^- + \mathrm{Cl}^- \qquad K_1 = k_1/k_{-1} \tag{1}$$

$$\mathrm{MoOCl_4}^- + \mathrm{NO_3}^- \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MoOCl_3NO_3}^- + \mathrm{Cl}^- \tag{2}$$

$$\mathrm{MoOCl_3NO_3}^- \xrightarrow{k_3} \mathrm{MoO_2Cl_2} + \mathrm{Cl}^- \tag{3}$$

Reaction 1 is a rapid equilibrium. Reaction 2 is the displacement of a second Cl^- by NO_3^- to form the $MoOCl_3NO_3^-$ complex. An intramolecular electron transfer of $MoOCl_3NO_3^-$ occurs in reaction 3 to produce the products. Application of the steady-state condition to $MoOCl_3NO_3^-$ leads to the rate expression

$$\mathrm{d[P]/d}t = \frac{k_2k_3[\mathrm{MoOCl_4}^-][\mathrm{NO_3}^-]}{k_3 + k_{-2}[\mathrm{Cl}^-]}$$

where P = products = MoO_2Cl_2 = NO_2. Assuming the absorbance at 315 nm measures the total Mo(V) concentration ($MoOCl_4^-$ + $MoOCl_5^{2-}$) leads to the rate expression

$$\mathrm{d[P]/d}t = -\mathrm{d[Mo(V)]/d}t = \frac{k_2k_3K_1[\mathrm{NO_3}^-][\mathrm{Mo(V)}]}{(k_3 + k_{-2}[\mathrm{Cl}^-])(K_1 + [\mathrm{Cl}^-])}$$

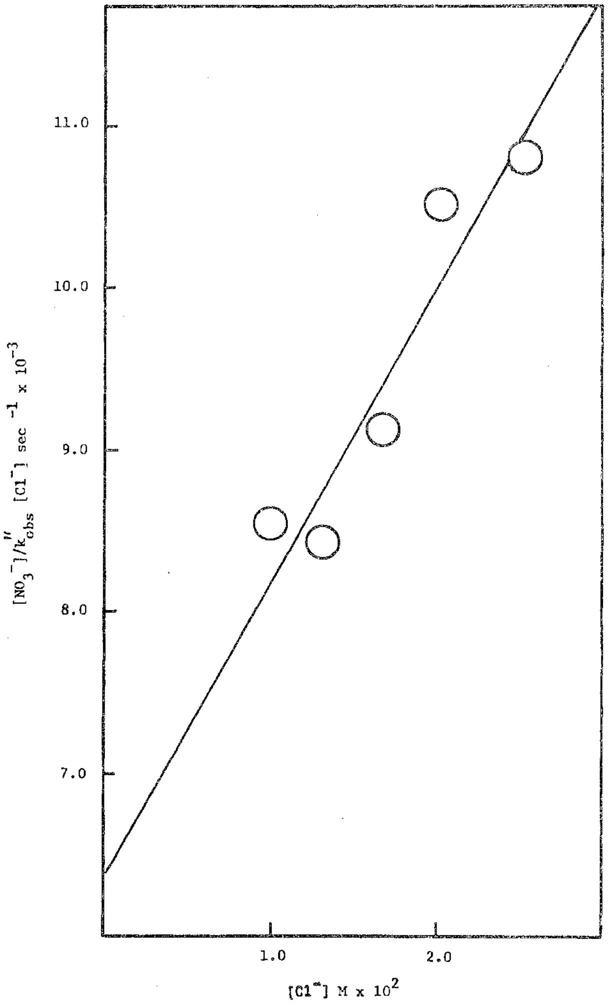

Figure 1. Plot of $[NO_3^-]/k''_{obsd}[Cl^-]$ vs. $[Cl^-]$ for runs with excess added Cl^- (25°).

If $k_3 \ll k_{-2}[Cl^-]$, this reduces to

$$-\mathrm{d[Mo(V)]/d}t = \frac{k_2k_3K_1[\mathrm{NO_3}^-][\mathrm{Mo(V)}]}{k_{-2}[\mathrm{Cl}^-](K_1 + [\mathrm{Cl}^-])} = \frac{k_3K_1K_2[\mathrm{NO_3}^-][\mathrm{Mo(V)}]}{[\mathrm{Cl}^-](K_1 + [\mathrm{Cl}^-])}$$

$$K_2 = k_2/k_{-2}$$

In the runs without added Cl^-, it is assumed that $K_1 \gg [Cl^-]$, which reduces the expression to a form which can be integrated

$$-\mathrm{d[Mo(V)]/d}t = \frac{k_3K_2[\mathrm{NO_3}^-][\mathrm{Mo(V)}]}{[\mathrm{Cl}^-]}$$

If $K_1 \gg [Cl^-]$, the initial $[Cl^-] \simeq$ initial $[(NH_4)_2MoOCl_5]$, and the integrated expression in the presence of excess NO_3^- is

$$2[\mathrm{Mo(V)}] - 3[\mathrm{Mo(V)}]_0 \ln [\mathrm{Mo(V)}] = k_3K_2[\mathrm{NO_3}^-]t + I$$

where $[Mo(V)]_0$ = initial $[(NH_4)_2MoOCl_5]$, *I* is the integration constant, and $k_{obsd} = k_3K_2[NO_3^-]$. For the runs with NO_3^- not in excess (second order), the integrated expression is

$$2 \ln (a + [\mathrm{Mo(V)}]) + \frac{3\,[\mathrm{Mo(V)}]_0}{a} \ln \frac{a + [\mathrm{Mo(V)}]}{[\mathrm{Mo(V)}]} = k_3K_2t + I$$

$$a = [\mathrm{NO_3}^-]_0 - [\mathrm{Mo(V)}]_0$$

$$k'_\mathrm{obsd} = k_3K_2$$

Table I. Rate Constants for the Reduction of NO_3^- by $(NH_4)_2MoOCl_5$

$10^4[(NH_4)_2MoOCl_5]_0$, M	$10^2[Et_4NNO_3]_0$, M	$10^2[NaNO_3]_0$, M	$10^2[NO_3^-]_0$,[a] M	$10^3[Et_4NNCl]$, M	T, °C	10^4k_{obsd}[b]/$[NO_3^-]_0$, sec^{-1}	$10^4 \cdot k'_{obsd}$,[c] sec^{-1}	$10^4k''_{obsd}$[d]$\cdot(K_1 + [Cl^-])\cdot[Cl^-]/K_1\cdot[NO_3^-]$, sec^{-1}
4.92		0.542	0.453		25	1.63		
4.26		0.620	0.508		25	1.43		
5.07		1.57	1.07		25	1.48		
3.23		0.729	.581		25	1.45		
4.40		1.77	1.17		25	1.36		
5.69		3.10	1.76		25	1.41		
4.93		3.51	1.92		25	1.50		
5.38		5.00	2.43		25	1.70		
4.66		5.67	2.64		25	1.63		
3.59		6.67	2.91		25	1.50		
6.10		4.33	2.21		25	1.70		
2.61		3.03	1.73		25	1.74		
4.46		3.03	1.73		25	1.63		
5.23		3.03	1.73		25	1.95		
6.00		3.03	1.73		25	1.51		
7.53		3.03	1.73		25	1.60		
7.99		3.03	1.73		25	1.71		
9.99		3.03	1.73		25	1.54		
4.46		0.155	0.155		25		1.64	
5.94		0.104	0.104		25		1.74	
5.69	5.24				25	1.74		
4.61	5.18			0.490	25	1.82		
4.61	5.18			1.12	25	1.80		
5.23	5.18			2.12	25	1.76		
5.23	5.18			4.35	25	1.66		
5.68	4.84			10.6	25			1.52
5.00	5.25			13.2	25			1.62
4.77	5.32			16.7	25			1.61
5.38	4.84			20.0	25			1.49
5.23	6.12			25.4	25			1.59
4.62	1.05				15	0.474		
5.53	1.11				30	2.61		
4.92	1.23				35	4.23		
4.00	1.26				40	6.57		
4.15	1.05				50	18.1		

[a] $[NO_3^-]_0$ calculated from ion-pair equilibrium. [b] $k_{obsd} = k_3K_2[NO_3^-]_0$. [c] $k'_{obsd} = k_3K_2$. [d] $k''_{obsd} = k_3K_1K_2[NO_3^-]/[Cl^-](K_1 + [Cl^-])$; $\Delta H^‡ = 18.3 \pm 0.4$ kcal mol^{-1}; $\Delta S^‡ = -14 \pm 2$ cal mol^{-1} K^{-1} (25°). $k_{obsd}/[NO_3^-]_0 = (1.63 \pm 0.15) \times 10^{-4}$ sec^{-1} (25°).

Plots of the data using these expressions are linear to >90% reaction and the values of the rate constants (k_3K_2) are consistent over the range of concentrations used (Table I).

When excess Cl^- is added, the rate expression becomes an ordinary psuedo-first-order expression, with $k''_{obsd} = k_3K_1K_2[NO_3^-]/[Cl^-](K_1 + [Cl^-])$. This may be rearranged to give

$$\frac{[NO_3^-]}{k''_{obsd}[Cl^-]} = \frac{[Cl^-]}{k_3K_1K_2} + \frac{1}{k_3K_2}$$

A plot of the left side of this equation vs. $[Cl^-]$ should be linear, with intercept $1/k_3K_2$ and slope $1/k_3K_1K_2$. This is in fact the case, as seen in Figure 1. Furthermore, the value of k_3K_2 obtained from the intercept ($(1.56 \pm 0.16) \times 10^{-4}$ sec^{-1}) is in excellent agreement with the value obtained from runs without added Cl^- ($k = (1.63 \pm 0.15) \times 10^{-4}$ sec^{-1}).

The value of K_1, evaluated from the slope of this plot is $(3.6 \pm 0.8) \times 10^{-2}$ M. This is in agreement with the assumption made in obtaining the integrated rate expression for runs in the absence of added Cl^- ($K_1 \gg [Cl^-]$ since $[Cl^-]$ in those runs never exceeds $\sim 1.5 \times 10^{-3}$ M. Furthermore, the value of K_1 indicates, at the concentration of $(NH_4)_2MOCl_5$ used, the dissociation in reaction 1 is essentially complete, in agreement with the assumption of $[Cl^-]_0 = [(NH_4)_2MoOCl_5]_0$ used in obtaining the integrated expression. The data, therefore, are consistent with the proposed mechanism over the range of concentrations used.

At high $[Cl^-]$, equilibrium 1 is displaced somewhat to the left, giving appreciable amounts of $MoOCl_2^{2-}$. The absorption band and the molar absorptivity (ϵ) at 315 nm of solutions of $(NH_4)_2MoOCl_5$ are insensitive to added Cl^-, however, indicating $MoOCl_5^{2-}$ and $MoOCl_4^-$ are indistinguishable at this wavelength. This was verified by synthesizing $NH_4MoOCl_4\cdot CH_3CN$[14] and comparing its spectrum in DMF with the spectrum of $(NH_4)_2MoOCl_5$ in DMF. At the concentration used ($\sim 10^{-3}$ M) the two are essentially identical. This is perhaps not surprising, since the Cl^- trans to oxygen in $MoOCl_5^{-2}$ is known to be weakly bound, and it has been reported that its substitution by various ligands has little effect on the spectrum.[18] Furthermore, recent work concerning $MoOCl_5^{2-}$ in nonaqueous solvents and in concentrated HCl indicates $MoOCl_4^-$ is the major species present.[19] Thus, the absorbance at 315 nm measures the total Mo(V) concentration, as required by the rate expression derived from the mechanism.

The activation parameters for the reaction, obtained from the Eyring plot of ln (k/T) vs. $1/T$, are found in Table I. The rather large negative activation entropy (−14 cal) suggests considerable increase in order in the transition state. If the mechanism is correct, however, the experimental $\Delta S^‡$ involves ΔS for reaction 2 ($k_{exptl} = k_3K_2$), which is unknown. Therefore, no conclusions concerning the origin of the entropy term may be drawn.

The biological reduction of nitrate may proceed by a mechanism similar to the one proposed here: a one-electron reduction of NO_3^- to NO_2 at a nonaqueous Mo(V) site followed by disproportionation of NO_2 to NO_3^- and NO_2^- in the aqueous environment after NO_2 is released by the enzyme. If the mechanism is correct, the rate constant for the actual electron-transfer reaction, k_3, must be considerably larger than k_{obsd}, since K_2 must be small. In the nitrate reductase enzymes, the preliminary displacement of a ligand by NO_3^- might either be unnecessary or be much more favorable, accounting for the rapid enzymatic reduction rates.

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Registry No. NO_3^-, 14797-55-8; $(NH_4)_2MoOCl_5$, 17927-44-5; DMF, 68-12-2.

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X-Ray Photoelectron Spectroscopic Study of Volatile Vanadium Compounds

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Vapor-phase core electron binding energies were determined by X-ray photoelectron spectroscopy for nine vanadium compounds. Vanadium $2p_{3/2}$ binding energies were correlated using CHELEQ atomic charges and the "transition-state" point charge potential equation. Excellent correlation was obtained for compounds which are well represented by a single valence-bond structure. In the case of the other compounds, information regarding the relative contributions of various resonance structures and the importance of back-bonding was obtained by comparison of experimental and calculated binding energies.

Introduction

The CHELEQ electronegativity equalization procedure for calculating atomic charges has been successfully used, in conjunction with the point charge potential equation, to correlate core electron binding energies for a wide range of simple organic and inorganic compounds.[1,2] The method has been parameterized for transition metal compounds and has been used to a limited extent for such compounds,[2,3] but no systematic study has been made of the applicability of the method outside the main-group elements. In this paper we report gas-phase core electron binding energies determined by X-ray photoelectron spectroscopy for nine vanadium compounds and we discuss the nature of the bonding in these compounds as deduced from the data. This work is the first gas-phase XPS study of a series of compounds of a transition metal in which a wide range of metal oxidation states is spanned.

Experimental Section

Standard high-vacuum and inert-atmosphere techniques were employed. The organometallic vanadium compounds were handled under argon. All metal and glassware used in manipulation of the vanadium halides and oxyhalides were flamed under high vacuum and pretreated with the compound to be handled. Vanadium pentafluoride was prepared by the thermal disproportionation of VF_4 (Orion) in a steel bomb.[4] The VF_5 was twice treated with activated NaF[5] and was stored in a bulb containing activated NaF. Vanadyl trifluoride (Alfa) was used without further purification. Vanadyl trichloride (ROC/RIC) was distilled through traps at 0, −78, and −196°. The clear liquid collected at −78° had a vapor pressure at 0° of 4.2 Torr (lit.[6] 4.4 Torr). Vanadium tetrachloride (Orion) was distilled through traps at 0, −78, and −196°. The dark red liquid collected at −78° was stored at −78° until used. Tris(hexafluoroacetylacetonato)vanadium,[7,8] V(hfacac)$_3$, was prepared by the method of Morris et al.[8] and purified by sublimation (mp 75.5–76.5°, lit.[7] 76°). The (π-C_5H_5)V(CO)$_4$ (Strem) (mp 139.5–140.5°, lit.[9] 139°) was used without further purification. Its infrared spectrum agreed with the literature.[9] Vanadium hexacarbonyl was prepared from [Na(diglyme)$_2$][V(CO)$_6$] (Orion) by the method of King.[10] It was stored in the dark at −78° over P_5O_5 and resublimed immediately before use. The (π-C_7H_7)V(CO)$_3$ was prepared from V(CO)$_6$ and cycloheptatriene by the method of Werner and Manastyrskyj[11] and was purified by sublimation. The product melted at 133–134° (lit.[11] 134–137°) and exhibited an infrared spectrum in agreement with the literature.[11] The (π-C_7H_7)V(π-C_5H_5) was prepared from (π-C_5H_5)V(CO)$_4$ and cycloheptatriene by the method of King and Stone[12] and was purified by sublimation at 120°.

X-Ray Photoelectron Spectra. Spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer.[13] The halides, oxyhalides, and vanadium hexacarbonyl were irradiated in a gold-plated chamber with a volume of 300 cm^3, a 0.5-mm exit slit, and an aluminum X-ray window. Tris(hexafluoroacetylacetonato)vanadium, (π-C_5H_5)V(CO)$_4$, and (π-C_7H_7)V(CO)$_3$ were irradiated using a slit plug described by Banna.[14] The sample and reference gas were handled in a system constructed of 0.5-in. stainless steel pipe. This system was assembled and secured while back-flushing with argon gas as in standard Schlenk manipulation. The vapor of the compound passed to the irradiation chamber through a 15-in. length of tubing constructed of Pyrex glass and stainless steel. The samples of VCl_4 and V(CO)$_6$ were held at 0° during data collection to minimize decomposition. The (π-C_7H_7)V(π-C_5H_5) was held in a heated chamber[14] at ca. 100°.

Magnesium Kα X-rays (1253.6 eV) were used for all spectra. Argon or neon at a partial pressure of 20–40 μ was introduced with the sample to the irradiation chamber, and the Ar $2p_{3/2}$ line (E_B = 248.45 eV) or the Ne 1s line (E_B = 870.21 eV) was used as a reference.