

Electrochemistry and Photoelectron Spectroscopy of Oxomolybdenum(V) Complexes with Phenoxide Ligands: Effect of *Para* Substituents on Redox Potentials, Heterogeneous Electron Transfer Rates, and Ionization Energies

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Complexes of the form $(\text{Tp}^*)\text{MoOCl}(\rho\text{-OC}_6\text{H}_4\text{X})$ and $(\text{Tp}^*)\text{MoO}(\rho\text{-OC}_6\text{H}_4\text{X})_2$ (Tp^* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate and X = OEt, OMe, Et, Me, H, F, Cl, Br, I, and CN) were examined by electrochemical techniques and gas-phase photoelectron spectroscopy to probe the effect of the remote substituent (X) on electron-transfer reactions at the oxomolybdenum core. Cyclic voltammetry revealed that all of these neutral Mo(V) compounds undergo a quasireversible one-electron oxidation ($\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$) and a quasireversible one-electron reduction ($\text{Mo}^{\text{V}}/\text{Mo}^{\text{IV}}$) at potentials that linearly depend on the electronic influence (Hammett σ_p parameter) of X. The first ionization energies for $(\text{Tp}^*)\text{MoO}(\rho\text{-OC}_6\text{H}_4\text{X})_2$ (X = OEt, OMe, H, F, and CN) were determined by photoelectron spectroscopy. A nearly linear correlation was found for the $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ oxidation potentials in solution and the gas-phase ionization energies. Calculated heterogeneous electron-transfer rate constants show a slight systematic dependence on the substituent.

Introduction

Molybdenum is associated with about fifty enzymes, which are essential to the metabolism of carbon, nitrogen, and sulfur by animals, plants, and microorganisms,¹ and crystal structures have been obtained for several molybdenum-containing enzymes.^{2–12} Catalysis by these enzymes involves a formal

two-electron oxidation or reduction of the substrate while the molybdenum center undergoes an oxidation state change between Mo(VI) and Mo(IV).¹³ Regeneration of the active site is believed to proceed via two sequential one-electron steps, generating a transient Mo(V) state. Understanding electron transfer reactions at oxomolybdenum centers can provide insight into the roles such centers play in catalytic reactions of molybdenum-containing enzymes. Well-characterized, closely related model complexes provide an opportunity to investigate the fundamental spectroscopic, electrochemical, and kinetic properties of the oxo–Mo core.

Oxo–Mo(V) centers can be stabilized by the tridentate hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (Tp^*).¹⁴ We have previously isolated and characterized a series of (Tp^*)–

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- (1) Hille, R. *Chem. Rev.* **1996**, *96*, 2757–2816.
- (2) Kisker, C.; Schindelin, H.; Pacheco, A.; Wehbi, W. A.; Garrett, R. M.; Rajagopalan, K. V.; Enemark, J. H.; Rees, D. C. *Cell* **1997**, *91*, 973–983.
- (3) Schindelin, H.; Kisker, C.; Huber, J.; Rajagopalan, K.; Rees, D. *Science* **1996**, *272*, 1615–1621.
- (4) Li, H.; Temple, C.; Rajagopalan, K. V.; Schindelin, H. *J. Am. Chem. Soc.* **2000**, *122*, 7673–7680.
- (5) Schneider, F.; Lowe, J.; Huber, R.; Schindelin, H.; Kisker, C.; Knablein, J. *J. Mol. Biol.* **1996**, *263*, 53–69.
- (6) McAlpine, A. S.; McEwan, A. G.; Bailey, S. *J. Mol. Biol.* **1998**, *275*, 613–623.
- (7) McAlpine, A. S.; McEwan, A. G.; Shaw, A. L.; Bailey, S. *J. Biol. Inorg. Chem.* **1997**, *2*, 634–643.
- (8) Bray, R. C.; Adams, B.; Smith, A. T.; Bennett, B.; Bailey, S. *Biochemistry* **2000**, *39*, 11258–11269.
- (9) Stewart, L. J.; Bailey, S.; Bennett, B.; Charnock, J. M.; Garner, C. D.; McAlpine, A. S. *J. Mol. Biol.* **2000**, *299*, 593–600.

- (10) Romao, M. J.; Archer, M.; Moura, I.; Moura, J. J. G.; LeGall, J.; Engh, R.; Schneider, M.; Hof, P.; Huber, R. *Science* **1995**, *270*, 1170–1176.
- (11) Huber, R.; Hof, P.; Duarte, R. O.; Moura, J. J. G.; Moura, I.; LeGall, J.; Hille, R.; Archer, M.; Romao, M. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8846–8851.
- (12) Boyington, J. C.; Gladyshev, V. N.; Khangulaov, S. V.; Stadtman, T. C.; Sun, P. D. *Science* **1997**, *275*, 1305–1308.
- (13) Rajagopalan, K. V. *Molybdenum and Molybdenum Containing Enzymes*; Coughlan, M., Ed.; Pergamon Press: New York, 1980; pp 243–272.
- (14) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

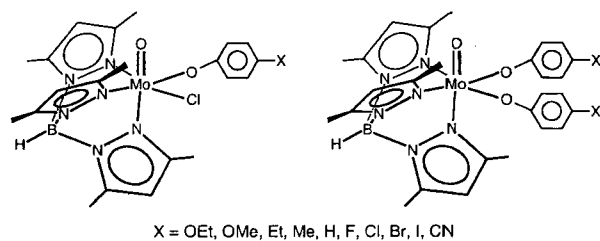


Figure 1. Structures of $(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{X})$ and $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$.

$\text{Mo}^{\text{V}}\text{O}(\text{X})(\text{Y})$ compounds in which the X and Y ligands were systematically varied to probe the effect of ligand substitution on the Mo center.¹⁵ Cyclic voltammetry demonstrated that the complexes undergo reversible one-electron reductions, and reduction potentials depended significantly upon the nature of the ligands.

Olson and Schultz performed electrochemical studies of $(\text{Tp}^*)\text{MoO}(\text{X})(\text{Y})$ complexes, where $\text{X}(\text{Y})$ is a bidentate ligand.¹⁶ Oxygen donor atoms were systematically replaced by sulfur donor atoms with the goal of correlating molecular structures to the electron transfer rates of the $\text{Mo}(\text{V}/\text{IV})$ reaction. Complexes with ligands attached via sulfur atoms exhibited more positive reduction potentials and faster electron transfer rates than those with oxygen atom ligation. They concluded that sulfur ligation of the oxo-Mo(V) center facilitates higher rates of electron transfer. However, since the reduction potentials for complexes with sulfur donor atoms are significantly larger than those for their oxygen donor counterparts, it is unclear whether the rate of electron transfer is primarily controlled by the nature of the donor atom or by other factors reflected in the electrochemical potentials of the system. Measuring heterogeneous electron-transfer rates using electrochemical methods amplifies the effects of reorganization energy because the driving force for electron transfer is zero under electrochemical conditions.^{17–20} Marcus theory predicts slower rates of electron transfer when large reorganization energies result from molecular rearrangements.^{21,22}

In this study, a series of $(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{X})$ and $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ complexes was investigated using electrochemistry and photoelectron spectroscopy (Figure 1). Within each series, the compounds differ only by the identity of the remote *para* substituent (X). Ranging from the electron-donating ethoxy groups to the electron-withdrawing cyano groups, the substituents are separated from the Mo core by an oxygen atom and a phenyl ring. All complexes exhibit reversible electrochemistry for both oxidation and

reduction of the Mo(V) center. Because Mo enzymes experience Mo(VI), Mo(V), and Mo(IV) states, it is important to investigate both the Mo(VI/V) and Mo(V/IV) couples. The volatility of the $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ compounds allows a comparison of solution phase oxidation potentials and gas-phase ionization energies measured by photoelectron spectroscopy. Photoelectron spectroscopic measurements are free from solvent complications and very fast relative to the experimental time scale of electrochemical techniques. This work shows that the electrochemical potentials are strongly dependent upon the nature of the remote substituent. The electron-transfer kinetics show a small but systematic dependence upon the potential. The correlation between the results from electrochemistry and photoelectron spectroscopy is presented.

Experimental Section

Materials. Reactions were conducted under an atmosphere of pure nitrogen gas. Solvents were purified by distillation as previously reported¹⁵ and thoroughly degassed before use. Subsequent product workup was performed in air. The progress of reactions and the purity of isolated compounds were monitored by thin-layer chromatography. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KTp^*) and dichloro[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]oxomolybdenum ($(\text{Tp}^*)\text{MoOCl}_2$) were prepared according to published procedures.^{15,23} Acetonitrile used for electrochemistry was purified by a triple distillation from CaH_2 , Li_2CO_3 and KMnO_4 , and P_2O_5 . Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and ferrocene were obtained from Aldrich Chemical Co.

Preparation of $(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{Me})$. A 0.31 g (2.2 mmol) portion of freshly prepared potassium salt of 4-methylphenol was added to 1.0 g (2.1 mmol) of $(\text{Tp}^*)\text{MoOCl}_2$ in 200 mL of benzene. The mixture was heated at 75 °C for 4 h. A color change from green to dark purple signaled completion, and the reaction mixture was cooled to room temperature. Unreacted materials were removed by filtration, and the filtrate was concentrated to ~2 mL for absorption chromatography on silica gel. The purple product was eluted with benzene and evaporated to dryness in vacuo. The yield was 45% based on Mo. The syntheses and characterization of all other compounds have been reported previously.^{24,25}

Electrochemical Measurements. Electrochemistry was performed on acetonitrile solutions (1–2 mM) over the potential range +2.0 to –1.8 V (vs Ag/AgCl) at a platinum-disk electrode (1.6 mm diameter) or platinum-disk microelectrode (100 μm diameter). The platinum-disk electrodes were polished with alumina prior to use. Solutions contained ~0.1 M Bu_4NBF_4 as the supporting electrolyte, and a platinum-wire auxiliary electrode was used. Cyclic voltammetry and chronocoulometry were conducted at room temperature with a Bioanalytical Systems (BAS) CV-50W potentiostat. Ferrocene was added to each solution upon completion of the experiments, and potentials are reported with respect to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Photoelectron Spectroscopy. Photoelectron spectra were recorded using a spectrometer with a 36 cm radius hemispherical analyzer (8 cm gap) and customized sample cells, excitation sources,

- (15) Cleland, W. E., Jr.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017–1025.
 (16) Olson, G. M.; Schultz, F. A. *Inorg. Chim. Acta* **1994**, *225*, 1–7.
 (17) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
 (18) Schultz, F. A. Private communication.
 (19) Brunschwig, B. S.; Sutin, N. *Coord. Chem. Rev.* **1999**, *187*, 233–254.
 (20) Sutin, N.; Brunschwig, B. S.; Creutz, C.; Winkler, J. R. *Pure Appl. Chem.* **1988**, *60*, 1817–1830.
 (21) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978.
 (22) Marcus, R. A. *Electrochim. Acta* **1968**, *13*, 995–1004.

- (23) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.
 (24) Chang, C. S. J.; Pecci, T.; Carducci, M.; Enemark, J. H. *Inorg. Chem.* **1993**, *32*, 4106–4110.
 (25) Chang, C. S. J. Ph.D. dissertation, The University of Arizona, Tucson, Arizona, 1991.

detection control, and data collection methods that have been previously described.²⁶ Ionization energy measurements were calibrated by the ${}^2E_{1/2}$ ionization of methyl iodide (9.538 eV), and the argon ${}^2P_{3/2}$ ionization (15.759 eV) was used as an internal energy scale lock. The instrument resolution was 0.015–0.025 eV. All samples sublimed cleanly with no evidence of decomposition. Sublimation temperature ranges were as follows: 198–200 °C for $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{OEt})_2$, 198–201 °C for $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{-Et})_2$, 185–190 °C for $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_5)_2$, 196–202 °C for $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{F})_2$, and 242–246 °C for $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{-CN})_2$. The data were fit using asymmetric Gaussians,²⁷ with positions reproducible to ± 0.02 eV ($\sim 3\sigma$ level).

Determination of Diffusion Coefficients and Heterogeneous Electron-Transfer Rate Constants. Cyclic voltammetry was used to determine electrochemical potentials for the oxidation and reduction of each sample. Chronocoulometry was performed over a range of pulse widths from 250 to 950 ms (in intervals of 100 ms) with the initial and final experimental potentials set on either side of the redox potential of interest. The slopes of the resulting Anson plots (charge versus square root of time) were averaged and used to calculate diffusion coefficients upon application of the Cottrell equation.²⁸ The value for the electrode area employed in these calculations (0.025 cm^2) was determined using chronocoulometric data for ferrocene and the known diffusion coefficient of ferrocene in acetonitrile.²⁹

For each redox reaction of interest, data from a series of cyclic voltammograms were recorded at scan rates ranging from 50 to 2100 mV/s (in intervals of 100 mV/s, excluding the measurement at 50 mV/s). As scan rates increase, the reaction is driven toward irreversibility, making the distance between anodic and cathodic peaks greater. Using the method developed by Nicholson, peak-to-peak separations (ΔE_p) were converted to a kinetic parameter (Ψ), and heterogeneous electron-transfer rate constants were calculated.^{30,31} Each experiment was repeated at least twice, and replicate measurements were in agreement. Error values were calculated by considering the error involved in very small mass measurements of the samples and the peak potential values reported by the BAS program.

Results and Discussion

Electrochemistry. Electrochemical reversibility and reduction potentials for Mo(VI/V) and Mo(V/IV) of the $(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{X})$ and $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ complexes were measured by cyclic voltammetry (CV). Cyclic voltammograms for all complexes displayed two well-resolved sets of peaks within the potential range ± 1.5 V (vs Ag/AgCl) corresponding to one-electron redox processes (Table 1). These reactions were determined to be quasireversible on the basis of the following criteria for reversibility: anodic and cathodic peak separation (ΔE_p) ~ 0.059 V; ratio of anodic and cathodic peak heights (i_{pa}/i_{pc}) ~ 1 ; and linear dependence of current flow on the square root of the scan

Table 1. Reduction Potentials (vs Fc/Fc⁺)^a

compound	X	Mo(VI/V)	Mo(V/IV)
		$E_{1/2}$, mV	$E_{1/2}$, mV
$(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{X})$	OEt	517.5	−1107.5
	OMe	530.0	−1101.0
	Et	702.0	−1092.0
	Me	708.0	−1080.0
	H	748.5	−1087.0
	F	789.5	−1042.0
	Cl	797.0	−1035.5
	Br	833.5	−1012.5
	I	837.5	−989.0
	CN	986.5	−881.0
$(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$	OEt	206.0	−1445.0
	OMe	214.0	−1434.0
	Et	301.0	−1429.0
	Me	302.0	−1417.0
	H	378.0	−1354.0
	F	396.0	−1328.0
	Cl	464.0	−1262.0
	Br	476.0	−1242.0
	I	485.0	−1225.0
	CN	664.5	−1032.5

^a Experimental conditions for cyclic voltammetry: Pt-disk electrode, 100 mV/s, 1–2 mM solutions of sample in 0.1 M Bu₄NBF₄/MeCN.

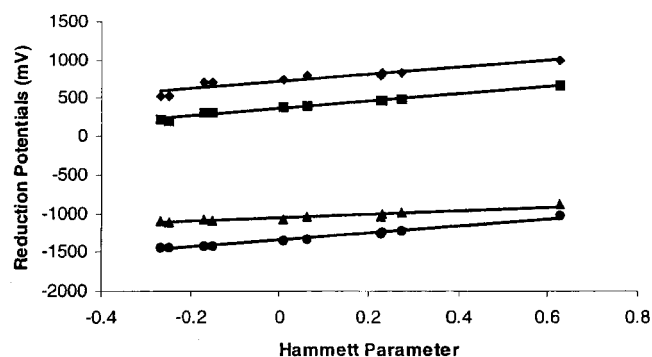


Figure 2. Correlation of reduction potentials (vs Fc/Fc⁺) and the Hammett parameter (σ_p) of X, increasing in the order of X = OEt, OMe, Et, Me, H, F, Cl, Br, I, and CN. $(\text{Tp}^*)\text{Mo}^{\text{VI/V}}\text{O}(\text{Cl})(\text{OC}_6\text{H}_4\text{X})$ (\blacklozenge); $(\text{Tp}^*)\text{Mo}^{\text{VI/V}}\text{O}(\text{OC}_6\text{H}_4\text{X})_2$ (\blacksquare); $(\text{Tp}^*)\text{Mo}^{\text{VI/V}}\text{O}(\text{Cl})(\text{OC}_6\text{H}_4\text{X})$ (\blacktriangle); $(\text{Tp}^*)\text{Mo}^{\text{VI/V}}\text{O}(\text{OC}_6\text{H}_4\text{X})_2$ (\bullet).

rate ($i_p/\nu^{1/2}$).^{28,32} Data for the complexes in this study approached theoretical values at slow scan rates (100 mV/s). The reversibility of these reactions indicates the absence of significant geometrical rearrangement within the complexes during redox activity. Structural changes resulting in irreversibility were observed by Schultz upon reduction of several seven-coordinate oxo–Mo(VI) systems.³³ The redox potentials ($E_{1/2}$, reported vs Fc/Fc⁺) represent the average of E_{pa} and E_{pc} .

Varying the remote *para* substituent on the phenoxide ligand has a profound effect on the observed redox potentials. Potentials increase linearly as a function of the Hammett parameter (σ_p), which serves as a measure of electronic influence of the substituent (Figure 2 and Supporting Information). Similar trends were observed by Jones and co-workers.³⁴ As a ligand becomes more electron-withdrawing,

(26) Westcott, B. L.; Gruhn, N. E.; Enemark, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3382–3386.

(27) Lichtenberger, D. L.; Copenhaver, A. S. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *50*, 335–352.

(28) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980.

(29) Kadish, K. M.; Ding, J. Q.; Malinkski, T. *Anal. Chem.* **1984**, *56*, 1741–1744.

(30) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351–1355.

(31) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

(32) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*; John Wiley & Sons: New York, 1995.

(33) Schultz, F. A. In *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J. A., Eds.; Kluwer Academic Publishers: Netherlands, 1993; pp 179–191.

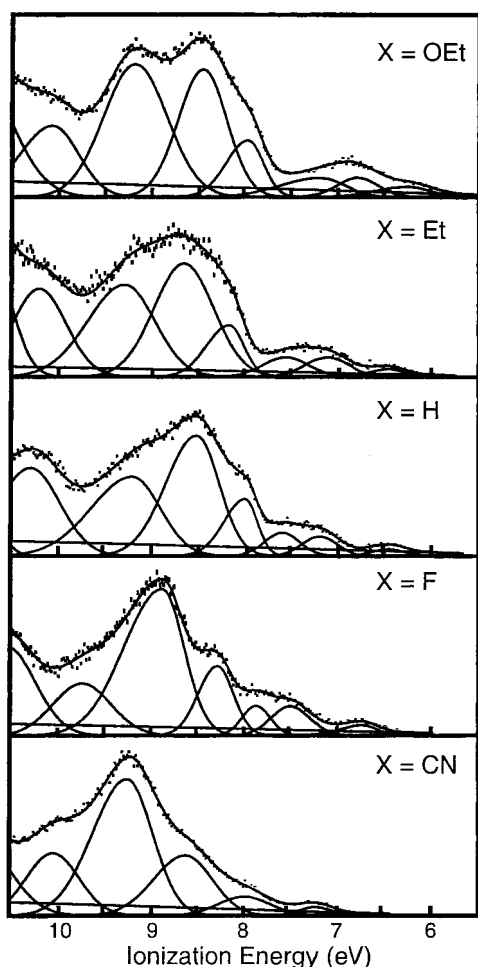


Figure 3. He I photoelectron spectra of $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$.

the decreased electron density at the Mo(V) center makes the complex easier to reduce and more difficult to oxidize. For the $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ complexes, the oxidation and reduction potentials increase by 0.4–0.5 V as the remote substituent is changed from OEt to CN. This sensitivity to the remote substituent is modest, however, compared to the changes observed for the Mo(V/IV) potential in $(\text{Tp}^*)\text{MoOY}_2$ complexes upon variation of the donor atom (Y), as reported by Cleland et al.¹⁵

The $(\text{Tp}^*)\text{MoOCl}(p\text{-OC}_6\text{H}_4\text{X})$ complexes exhibit more positive electrochemical potentials than the corresponding $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ complexes (Table 1 and Figure 2). Previous work has shown that attaching a third row element to an oxo–Mo center in place of a second row element (such as substitution of Cl for $\text{OC}_6\text{H}_4\text{X}$ in these systems) increases the Mo reduction potentials.^{15,35–37}

Photoelectron Spectroscopy. He I photoelectron spectra of $(\text{Tp}^*)\text{MoO}(p\text{-OC}_6\text{H}_4\text{X})_2$ complexes, where X = OEt, Et, H, F, and CN, were obtained and are shown from 11 to 5.5 eV (Figure 3). The assignments of ionization bands were

made by comparison to the spectra of previously studied $(\text{Tp}^*)\text{MoO}(\text{OR})_2$ compounds. For example, the spectrum of $(\text{Tp}^*)\text{MoO}(\text{OEt})_2$ contains a well-separated ionization at 6.58 eV attributed to a d^1 metal-based orbital, specifically, the highest occupied molecular orbital (HOMO) of the Mo(V) complex.³⁸ $(\text{Tp}^*)\text{MoO}(\text{OEt})_2$ and analogous alkoxides share a common band structure from 11 to 8 eV that is associated primarily with Tp^* ligand-based orbitals.

The $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_5)_2$ spectrum displays a leading metal-based ionization at 6.45 eV and a ligand-based band structure from 11 to 8 eV similar to that of $(\text{Tp}^*)\text{MoO}(\text{OEt})_2$. In addition, the spectrum also displays a band between the metal-based and (Tp^*) ligand-based ionizations. This band is best modeled with two Gaussians located at 7.16 and 7.58 eV, which are assigned to ionizations from in-phase and out-of-phase combinations of the highest occupied, primarily phenyl-based b_1 orbitals of the phenoxide ligands.

Significant differences are observed in the spectra of $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_4\text{OEt})_2$, $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_4\text{Et})_2$, and $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_5)_2$ below 8 eV, while the shape of the ionization profile above 8 eV remains relatively constant. The metal-based and phenoxide-based ionizations merge together and are observed at lower energies upon increased electron-donating ability of the remote substituent. This occurs because primarily phenyl-based ionizations are more influenced by remote substituents and destabilized to a greater extent than ionization of the d^1 metal-based orbital for each complex.

The three ionization bands of interest are all stabilized for $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_4\text{F})_2$. Fluorine's high electronegativity makes the removal of an electron more difficult. This electron-withdrawing effect is offset, however, by the π -donor ability of fluorine.³⁹ Thus, shifts to higher energy within the spectrum are smaller than would be predicted based on electronegativity alone. The spectrum for $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_4\text{-CN})_2$ displays band shifts to even higher energies due to the strong electron-withdrawing ability of the cyano substituents, and the most stable of these three ionizations has been shifted under the Tp^* ionizations and can no longer be observed.

Correlation of Electrochemistry and Photoelectron Spectroscopy. Results from both electrochemistry and photoelectron spectroscopy indicate that it is more difficult to remove an electron from $(\text{Tp}^*)\text{MoO}(\text{OC}_6\text{H}_4\text{X})_2$ compounds as the electron-withdrawing ability of the remote substituent increases. Mo(VI/V) electrochemical potentials and gas-phase ionization energies increase in the following order: OEt < Et < H < F < CN. Unlike solution phase electrochemistry, photoelectron spectroscopy provides gas-phase ionization data that are independent of solvent effects. In addition, the relatively short time scale of the photoelectron spectroscopy experiment inhibits ligand rearrangement. Despite the significant differences between these two techniques, the oxidation potentials and ionization energies correlate in a nearly linear manner (Figure 4 and Supporting

(34) Jones, C. J. Private communication.

(35) Chang, C. S. J.; Enemark, J. H. *Inorg. Chem.* **1991**, *30*, 683–688.

(36) Chang, C. S. J.; Collison, D.; Mabbs, F. E.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 2261–2267.

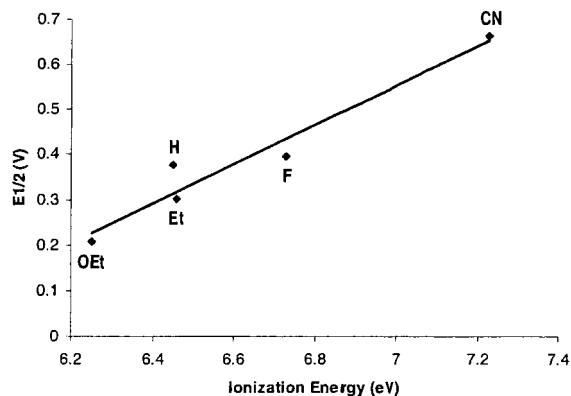
(37) Joshi, H. K.; Gruhn, N. E.; Lichtenberger, D. L.; Enemark, J. H. *Abstracts*, National Meeting of the American Chemical Society, San Diego, CA, April, 2001; INOR 209.

(38) Chang, C. S. J.; Rai-Chaudhuri, A.; Lichtenberger, D. L.; Enemark, J. H. *Polyhedron* **1990**, *9*, 1965–1973.

(39) Fagnou, K.; Lautens, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 26–47.

Table 2. Diffusion Coefficients (D_0) and Heterogeneous Electron Transfer Rate constants (k_s) for Representative Complexes

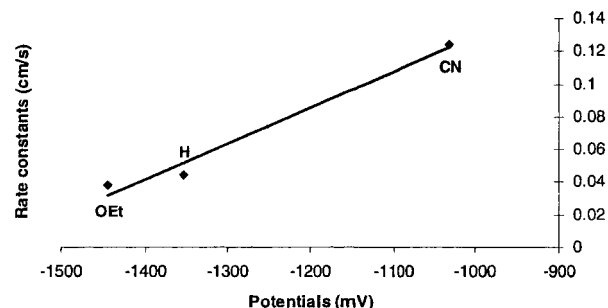
compound	Mo(VI/V) D_0 ($\times 10^{-5}$ cm ² /s); k_s (cm/s)	Mo(V/IV) D_0 ($\times 10^{-5}$ cm ² /s); k_s (cm/s)
(Tp*)MoOCl(<i>p</i> -OC ₆ H ₄ OEt)	3.46 \pm 0.90; 0.039 \pm 0.015	2.04 \pm 0.20; 0.015 \pm 0.003
(Tp*)MoOCl(<i>p</i> -OC ₆ H ₅)	6.42 \pm 3.09; 0.043 \pm 0.020	2.77 \pm 1.33; 0.030 \pm 0.005
(Tp*)MoOCl(<i>p</i> -OC ₆ H ₄ CN)	9.64 \pm 2.83; 0.126 \pm 0.098	3.68 \pm 1.35; 0.067 \pm 0.026
(Tp*)MoO(<i>p</i> -OC ₆ H ₄ OEt) ₂	1.99 \pm 0.50; 0.082 \pm 0.034	5.37 \pm 1.35; 0.038 \pm 0.011
(Tp*)MoO(<i>p</i> -OC ₆ H ₅) ₂	4.10 \pm 1.40; 0.090 \pm 0.033	5.58 \pm 1.90; 0.044 \pm 0.013
(Tp*)MoO(<i>p</i> -OC ₆ H ₄ CN) ₂	3.48 \pm 0.61; 0.161 \pm 0.065	1.78 \pm 0.31; 0.124 \pm 0.052

**Figure 4.** Correlation of (Tp*)MoO(*p*-OC₆H₄X)₂ electrochemical potentials of Mo^{VI/V} (vs Fc/Fc⁺) and ionization energies.

Information). This indicates that the presence of solvent does not greatly influence the relative electrochemical measurements of these systems.

Kinetics of Heterogeneous Electron Transfer. Using cyclic voltammetric and chronocoulometric data collected for (Tp*)MoOCl(*p*-OC₆H₄X) and (Tp*)MoO(*p*-OC₆H₄X)₂, where X = CN, H, and OEt, diffusion coefficients and rate constants were calculated for the Mo(VI/V) and Mo(V/IV) reactions (Table 2). The compounds with X = OEt and X = CN bracket the extremes of the potentials for each series. The diffusion coefficients range from 10⁻⁶ to 10⁻⁵ cm²/s, similar to those of Olson and Schultz,¹⁶ and appear to be independent of the nature of the remote substituent within the precision of the measurements. The rate constants for heterogeneous electron transfer reactions of Mo(VI/V) and Mo(V/IV) are consistently smaller for (Tp*)MoOCl(*p*-OC₆H₄X) compared to the corresponding (Tp*)MoO(*p*-OC₆H₄X)₂ compounds. Mo(VI/V) rate constants are all slightly larger than those for Mo(V/IV), but all of the values are within an order of magnitude of each other. Within each series, the rate constants increase systematically with $E_{1/2}$ (Figure 5 and Supporting Information).

Olson and Schultz previously observed that the Mo(V/IV) process is faster (10-fold increase in apparent rate constant) and the reduction potential is ~600 mV more positive upon substitution of sulfur donor atoms for oxygen donor atoms in the 1,2-disubstituted benzene ligand.¹⁶ We have further investigated the controlling factors in heterogeneous electron transfer kinetics by studying a series of compounds of similar shape and size with identical donor atoms, but whose reduction potentials vary significantly because of the electronic influence of the remote substituents. More positive reduction potentials lead to mildly faster electron transfer. For example, a ~410 mV potential difference within the (Tp*)Mo^{VI/IV}O(*p*-OC₆H₄X)₂ series is associ-

**Figure 5.** Correlation of representative (Tp*)Mo^{VI/IV}O(*p*-OC₆H₄X)₂ (X = OEt, H, and CN) heterogeneous rate constants with the reduction potentials (vs Fc/Fc⁺).

ated with a 3-fold larger apparent rate constant (Figure 5). These rate constant differences are much greater than those caused by the electrical double layer effect at the electrode surface.⁴⁰ Thus, this work shows that electrochemical potential has a detectable effect on the kinetics of electron transfer for these closely related oxomolybdenum compounds.

Several systems have been reported in which redox potentials and heterogeneous electron-transfer rates of metal-centered complexes are influenced in a parallel manner by donor atoms and substituent groups.^{16,18,41-43} For oxo-Mo-(catecholate) compounds (which have oxygen donor atoms), the electrochemistry depends significantly on the substituents of the catecholate ligand.^{41,43} When the metal coordination environment is essentially constant, the inner-shell reorganization energy comprises the largest barrier to electron transfer within the complex. Slow electron transfer rates imply substantial rearrangement among the metal-ligand bonds during electron transfer. It has been proposed that electron-donating substituents create a more electrostatic bond with the metal, making redox potentials more negative and electron-transfer slower because of the increased activation barrier.^{43,44} Our electrochemical study of (Tp*)MoOCl(*p*-OC₆H₄X) and (Tp*)MoO(*p*-OC₆H₄X)₂ is consistent with this suggestion. The complexes with more positive reduction potentials have electron-withdrawing remote substituents and exhibit faster heterogeneous electron-transfer rates for both the Mo(VI/V) and Mo(V/IV) processes.

(40) Delahay, P. *Double Layer and Electrode Kinetics*; John Wiley & Sons: New York, 1965.

(41) Mondal, J. U.; Zamora, J. G.; Siew, S.; Garcia, G. T.; George, E. R.; Kinon, M. D.; Schultz, F. A. *Inorg. Chim. Acta* **2001**, *321*, 83-88.

(42) Lexa, D.; Saveant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235-243.

(43) Schultz, F. A. *J. Electroanal. Chem.* **1986**, *273*, 169-174.

(44) Fukuzumi, S.; Nakanishi, I.; Tanaka, K.; Suenobu, T.; Tabard, A.; Guillard, R.; Van Caemelbecke, E.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 785-790.

Summary

The remote substituent of the investigated (Tp*)MoOCl(*p*-OC₆H₄X) and (Tp*)MoO(*p*-OC₆H₄X)₂ complexes has a significant effect on their electrochemistry and gas phase photoelectron spectroscopy. Electron-donating substituents make the Mo(V) center more difficult to reduce by adding electron density to the metal. Compounds with electron-withdrawing substituents are easier to reduce, as shown by their more positive reduction potentials. The mono-phenoxy complexes are easier to reduce and more difficult to oxidize than the corresponding bis-phenoxy complexes because of the presence of the chloride ligand attached to the oxo-Mo(V) core in place of the oxygen donor group. Gas-phase photoelectron spectroscopy allows one to observe how these complexes behave in the absence of other chemical species. A nearly linear correlation exists for the first ionization energies in the gas phase and the Mo(VI/V) oxidation potentials in solution, indicating that solvent effects are negligible in these electrochemical measurements.

The rate constants for heterogeneous electron transfer show a slight but significant systematic dependence upon reduction potential for all four types of one-electron reactions studied. These results for a series of oxo-Mo(V) complexes with common donor atoms and stereochemistry are consistent with the original proposal of Schultz and Olson¹⁶ that the nature of the donor atom to the oxo-Mo(V) center primarily controls the rate of heterogeneous electron transfer in these systems. However, this work has also shown that potential differences of 400–500 mV can produce a 3-fold change in electron-transfer rates. The reduction potentials of molybdenum enzymes that are presumed to have the same coordination environment can vary significantly. For ex-

ample, the Mo(V/IV) couples of sulfite oxidase and plant nitrate reductase from eukaryotes, which both belong to the sulfite oxidase structural family, differ by ~200 mV at pH 7.¹ Thus, changes in the potentials of oxo-Mo centers of enzymes may have significant effects on the rates of electron transfer that are an integral part of their catalytic cycles. Additional quantitative studies of electron-transfer reactions of molybdenum and tungsten centers with a variety of donor atoms and remote substituents are in progress to further elucidate this possibility.

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Supporting Information Available: Regression analyses for the correlations of reduction potentials with the Hammett parameter, ionization energies, and electron-transfer rate constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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