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Article

Modulation of Molybdenum-Centered Redox Potentials and Electron-Transfer Rates by Sulfur versus Oxygen Ligation

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Temperature-dependent measurements of potential, $E^{\circ\prime}$, and electron-transfer rate constant, $k_{s,h}$, are reported for electrochemical reduction (in 0.3 M $TBAPF_6/CH_3CN$) of a series of oxomolybdenum(V) complexes, [(Tp*)MoO(X,Y)], where Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate and X,Y is a series of bidentate 1,2-disubstituted aliphatic or aromatic ligands in which oxygen donors are replaced sequentially by sulfur. $E^{\circ\prime}$ values shift in the positive direction, and $k_{s,h}$ values increase as O is replaced by S and as the framework of the ligand is changed from aliphatic to aromatic. The electrochemical enthalpy of activation, measured under conditions of zero driving force as $\Delta H^{\ddagger} = -R\,\partial[\ln(k_{s,h})]/\partial(1/T)$ and corrected for an outer-shell component by the mean spherical approximation, is ~10 kJ mol^{-1} larger for complexes with O versus S donors and with an aliphatic versus aromatic ligand framework. Thus, the rate of $Mo^{V/IV}$ electron transfer is modulated primarily by differences in inner-shell reorganization. Following a recent description of electronic structure contributions to electron-transfer reactivity (Kennepohl, P.; Solomon, E. I. *Inorg. Chem.* **2003**, *42*, 679 ff), it is concluded that more effective charge distribution over the entire molecular structure, as mediated by electronic relaxation in S versus O and aromatic versus aliphatic systems, is responsible for the influence of ligand structure on the kinetics and thermodynamics of Mo-centered electron transfer. There is no evidence, based on experimentally measured pre-exponential factors, that sulfur donors or an aromatic ligand framework are more effective than their structural counterparts in facilitating electronic coupling between the electrode and the Mo d_{xy} redox orbital.

Introduction

The active sites of oxomolybdenum enzymes contain one or two ene-1,2-dithiolate ligands and, in many cases, a terminal sulfide and/or cysteine thiolate.[1,2] These sulfur donors appear to be crucial to enzyme reactivity. Of particular interest is the possibility that Mo−S orbital overlap provides an effective low-energy pathway for electron transfer to and from the metal.[3] There is evidence from spectroscopic and computational model compound studies that a three-center, pseudo-σ overlap is created by interaction of the filled in-plane S orbitals of coordinated enedithiolate(s) with the Mo d_{xy} redox orbital.[4] In addition, folding of a coordinated enedithiolate along its S···S vector[5] or rotation of a saturated thiolate about its Mo−S bond[6] can produce strong Mo d_{xy}−S 3p π interactions. On the basis of spatial extent and the energy match of S with Mo orbitals, it is presumed that these interactions create a means of modulating the thermodynamics and kinetics of electron transfer.

In recent years, we[7] and others[8] have explored the influence of sulfur coordination on molybdenum-centered electron transfer through electrochemical studies of com-

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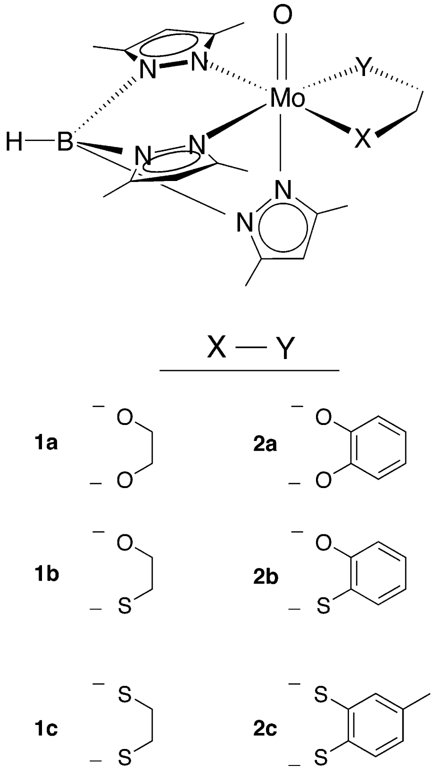
Chart 1



pounds such as those shown in Chart 1. Systematic substitution of S for O produces a positive shift in $E°'$ (the potential of $Mo^{V/IV}$ reduction) and an increase in $k_{s,h}$ (the heterogeneous electron-transfer rate constant). Thermodynamic modulation of Mo(IV) stability by Mo−S covalency frequently is proposed as an explanation for the influence of sulfur coordination on $E°'$.[9] However, the origins of the kinetic differences are less well understood. One explanation is that the larger force constants of Mo−O versus Mo−S bonds should produce larger inner-shell reorganizations accompanying reduction and result in smaller values of $k_{s,h}$. A second possibility is that the greater covalency of Mo−S versus Mo−O bonds produces larger electron transfer rates via more effective electronic coupling with the metal. The latter consequence would be reflected in relative values of the pre-exponential factor in the rate law, which will be larger for electron transfer reactions that are fully adiabatic compared to those that are not. Nonadiabatic electrochemical behavior has been claimed for a number of oxygen-rich reactants.[10−12] Specifically, Maran et al. have produced evidence that the dissociative electron-transfer reductions of organic peroxides and peresters, which are characterized by small values of $k_{s,h}$ and unusually low pre-exponential factors, are strongly nonadiabatic.[10] Related sulfur-containing molecules do not exhibit such behavior.[13]

In this paper, we explore the basis of enhanced Mo−S versus Mo−O reactivity through temperature-dependent measurements of $E°'$ and $k_{s,h}$ for the following electrode reaction:

$$[(\mathrm{Tp}^*)\mathrm{Mo}^{\mathrm{V}}\mathrm{O}(\mathrm{X,Y})] + e^- \leftrightarrows [(\mathrm{Tp}^*)\mathrm{Mo}^{\mathrm{IV}}\mathrm{O}(\mathrm{X,Y})]^- \quad E°', k_{s,h} \tag{1}$$

Here, Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate,[14] and 1-X,Y and 2-X,Y are a series of bidentate 1,2-disubstituted aliphatic and aromatic ligands, in each of which O donors are replaced sequentially by S to produce the oxomolybdenum(V) complexes **1a**−**c** and **2a**−**c** in Chart 1. Temperature-dependent measurements are carried out in acetonitrile solvent by use of cyclic voltammetry and the nonisothermal cell technique of Weaver,[15] in which $k_{s,h}$ is determined under conditions of zero driving force at the operative value of $E°'$. Results are interpreted in terms of classical Marcus theory for heterogeneous electron transfer[16]

$$k_{s,h} = Z_{het} \cdot \kappa_{el} \cdot \exp[-\Delta G^{\ddagger}/RT] \tag{2}$$

where $Z_{het} = (kT/2\pi m)^{1/2}$ is the collisional frequency factor with m = molecular mass, κ_{el} = the electronic transmission coefficient, and $\Delta G^{\ddagger}$ = the free energy of activation. To assess the "real" activation parameters, which are derived from temperature-dependent measurements of $k_{s,h}$ at zero driving force,[17] eq 2 is expressed as

$$k_{s,h} = Z_{het} \cdot \kappa_{el} \cdot \exp[\Delta S^{\ddagger}/R] \cdot \exp[-\Delta H^{\ddagger}/RT] = A_{het} \cdot \exp[-\Delta H^{\ddagger}/RT] \tag{3}$$

where $\Delta S^{\ddagger}$ is the apparent entropy of activation and $\Delta H^{\ddagger} = \Delta H^{\ddagger}_{is} + \Delta H^{\ddagger}_{os}$ is the sum of the inner- and outer-shell enthalpies of activation. It is anticipated that rate effects arising from differences in nuclear reorganization will be reflected in the relative values of $\Delta H^{\ddagger}$, whereas those arising from differences in electronic coupling will be reflected in the relative magnitudes of A_{het}. In the following sections,

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we report and comment on values of $\Delta H^{\ddagger}$ and A_{het} obtained for electrochemical reduction of compounds **1a**−**c** and **2a**−**c**.

Experimental Section

Materials. Complexes **1a**−**c** and **2a**−**c** were prepared and purified by previously described methods.[7,8a] The acetonitrile solvent for electrochemical experiments was obtained as distilled-in-glass reagent from Burdick and Jackson and put through three freeze−pump−thaw cycles and purged with Ar prior to use. Tetra-*n*-butylammonium hexafluorophospate (TBAPF$_6$) supporting electrolyte was obtained either from SACHEM and used as received or from G. F. Smith Chemical Company. The latter material was recrystallized from ethanol−water and dried in vacuo for 24 h at 100 °C prior to use.

Electrochemical Measurements. Electrochemical experiments were conducted in CH$_3$CN containing 0.3 M TBAPF$_6$. Solutions were deoxygenated with and maintained under a blanket of argon. Measurements were performed by use of a Bioanalytical Systems (BAS) CV-50W potentiostat and employed a three-electrode cell configuration consisting of a 1.6-mm (0.020 cm^2) or 250-μm (0.00049 cm^2) diameter Pt disk working electrode, a BAS Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. The 1.6-mm diameter electrode was purchased from BAS; the 250-μm diameter electrode was constructed locally by published methods.[18] Working electrodes were polished with an aqueous slurry of alumina (Buehler), rinsed with H$_2$O and solvent, and dried before use.

Temperature-dependent measurements were conducted in a nonisothermal electrochemical cell,[15] in which the working and reference electrode compartments were thermostated independently by circulating water baths. The reference compartment was maintained at 24 °C, and the temperature of the working compartment was varied from −20 to 24 °C. Temperature-dependent values of the specific resistivity, ρ, of 0.3 M TBPAF$_6$/CH$_3$CN solutions were taken from ref 19. Temperature-dependent values of diffusion coefficients, D, were determined by chronocoulometry.[20] Values obtained for **1a** and **2a** were used for all members of the respective series of compounds. Thus, for **1a**−**c**, $\ln D = -6.96 - 1203/T$ ($D = 1.67 \times 10^{-5}$ cm^2 s^{-1} at 297 K), and for **2a**−**c**, $\ln D = -5.38 - 1756/T$ ($D = 1.27 \times 10^{-5}$ cm^2 s^{-1} at 297 K).

Electrode kinetic parameters were determined from the sweep rate dependence of cyclic voltammetric peak potential separations, ΔE_p, using strategies described previously.[7,19,21] Peak potential separations were corrected for the influences of uncompensated solution resistance (R_u) and nonlinear diffusion by subtracting the quantities $(\Delta E_p)_{iR} = 2 \times i_p R_u$ (i_p = peak current, $R_u = 4\rho/r$, ρ = specific resistivity, r = electrode radius) and $(\Delta E_p)_{\mathrm{edge}}$ (obtained from tabulations of Heinze[22]) from the measured values of ΔE_p. Values of $k_{s,h}$ were obtained from previously published tabulations of ΔE_p versus the kinetic parameter $\psi = k_{s,h}/(\pi D F v/RT)^{1/2}$ in cases where $\Delta E_p < 200$ mV.[22,23] Beyond this limit, $k_{s,h}$ was calculated from the expression[24]

$$k_{s,h} = 2.18(\alpha^{\beta}\beta^{\alpha}FDv/RT)^{1/2}\exp(-\alpha\beta F\Delta E_p/RT) \qquad (4)$$

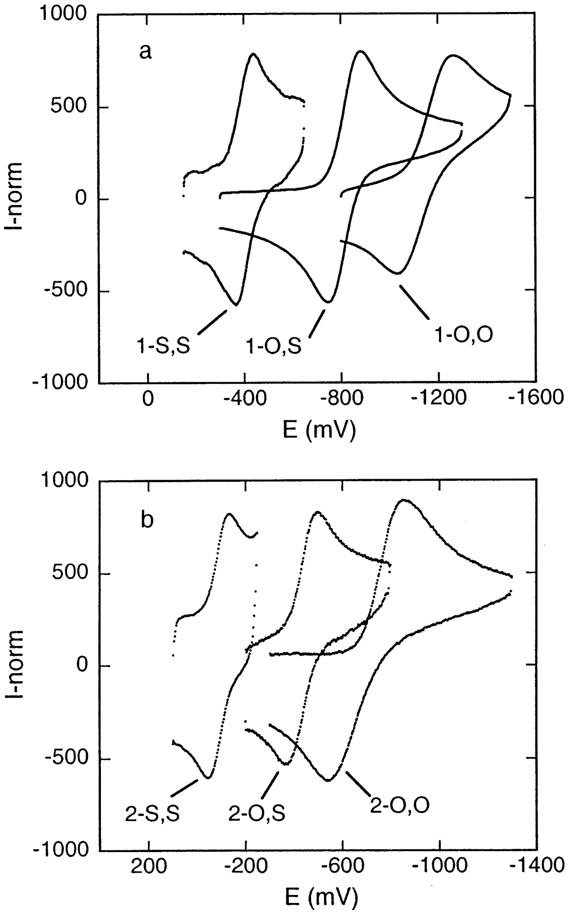

Figure 1. Normalized current cyclic voltammograms in 0.3 M TBAPF$_6$/CH$_3$CN for reduction of (a) [(Tp*)MoO(1-X,Y)] complexes at 297 K and $v = 5$ V s^{-1}; reactant concentration and electrode diameters are 0.5 mM, 1.6 mm (1-O,O); 1.5 mM, 250 μm (1-O,S); 1.7 mM, 250 μm (1-S,S) and (b) [(Tp*)MoO(2-X,Y)] complexes at 253 K and $v = 34$ V s^{-1}; reactant concentration and electrode diameters are 2.0 mM, 250 μm (2-O,O); 1.1 mM, 250 μm (2-O,S); 0.5 mM, 250 μm (2-S,S). I-norm = $i/v^{1/2}AC$, where i is current in μA, v is scan rate in V s^{-1}, A is electrode area in cm^2, and C is reactant concentration in mM.

where $\alpha = (1 - \beta) = 0.50$ is the transfer coefficient. Positive feedback compensation of solution resistance was not employed. Rather, conditions of reactant concentration (C = 0.2−1 mM), electrode size (r = 800 or 125 μm), and scan rate (v = 0.02−50 V s^{-1}) were controlled to keep corrections to ΔE_p to $\leq$10 mV in all cases.

Results

The cyclic voltammetric behavior of complexes **1a**−**c** and **2a**−**c** at constant temperature is illustrated in Figure 1. Each process is assigned to the diffusion-controlled, metal-centered, one-electron reaction described by eq 1 on the basis of a linear i_p versus $v^{1/2}$ response and a reverse-to-forward peak current ratio of ~1. Substitution of S for O in 1-X,Y and 2-X,Y produces large changes in electrochemical behavior. Redox potentials shift in the positive direction by 0.6−0.7 V, and electron-transfer rate constants increase significantly on the basis of changes in ΔE_p. There is about a 30-fold enhancement in $k_{s,h}$ for compounds **1a**−**c** and a

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Table 1. Electrochemical Data for Reduction of (Tp*)MoO(1-X,Y) and (Tp*)MoO(2-X,Y)[a]

complex	bidentate ligand	$E^{\circ\prime}_{297}$ (V)	ΔS°_{rc} (J mol^{-1} K^{-1})	$k_{s,h}^{297}$ (cm s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta H^{\ddagger}_{is}$[b] (kJ mol^{-1})	ln A_{het}	A_{het} (cm s^{-1})
1a	1-O,O	−1.145	−28(30)	0.0077	36(8)	17	9.5(3.6)	1.3×10^4
1b	1-O,S	−0.813	−53(6)	0.028	35(5)	16	10.7(2.6)	4.4×10^4
1c	1-S,S	−0.402	−42(5)	0.24	27(4)	8	9.4(1.6)	1.2×10^4
2a	2-O,O	−0.721	−48(4)	0.026	23(3)	8	5.5(1.4)	2.5×10^2
2b	2-O,S	−0.445	−26(7)	0.16	14(2)	−1	3.9(0.9)	0.5×10^2
2c	2-S,S	−0.112	−50(5)	0.31	13(1)	−2	3.9(0.1)	0.5×10^2

[a] In 0.3 M TBAPF$_6$/CH$_3$CN at a Pt electrode. [b] $\Delta H^{\ddagger}_{is} = \Delta H^{\ddagger} - \Delta H^{\ddagger}_{os}$, where $\Delta H^{\ddagger}_{os}$ is evaluated by use of eq 5 with values of $\epsilon_{op} = 1.800$, $\epsilon_s = 37.5$, and $\partial\epsilon_{op}/\partial T = -0.00121$ K^{-1} from ref 26; values of $\partial\epsilon_s/\partial T = -0.160$ K^{-1}, $\delta_s = 41.0$ pm, and $\partial\delta_s/\partial T = 0.094$ pm K^{-1} from ref 27; and values of $r = 380$ and 500 pm for compounds **1a**−**c** and **2a**−**c**, respectively. Reactant radii are evaluated by use of the Stokes−Einstein equation ($D = kT/6\pi\eta r$) with $\eta = 3.4 \times 10^{-4}$ Pa s (ref 26).

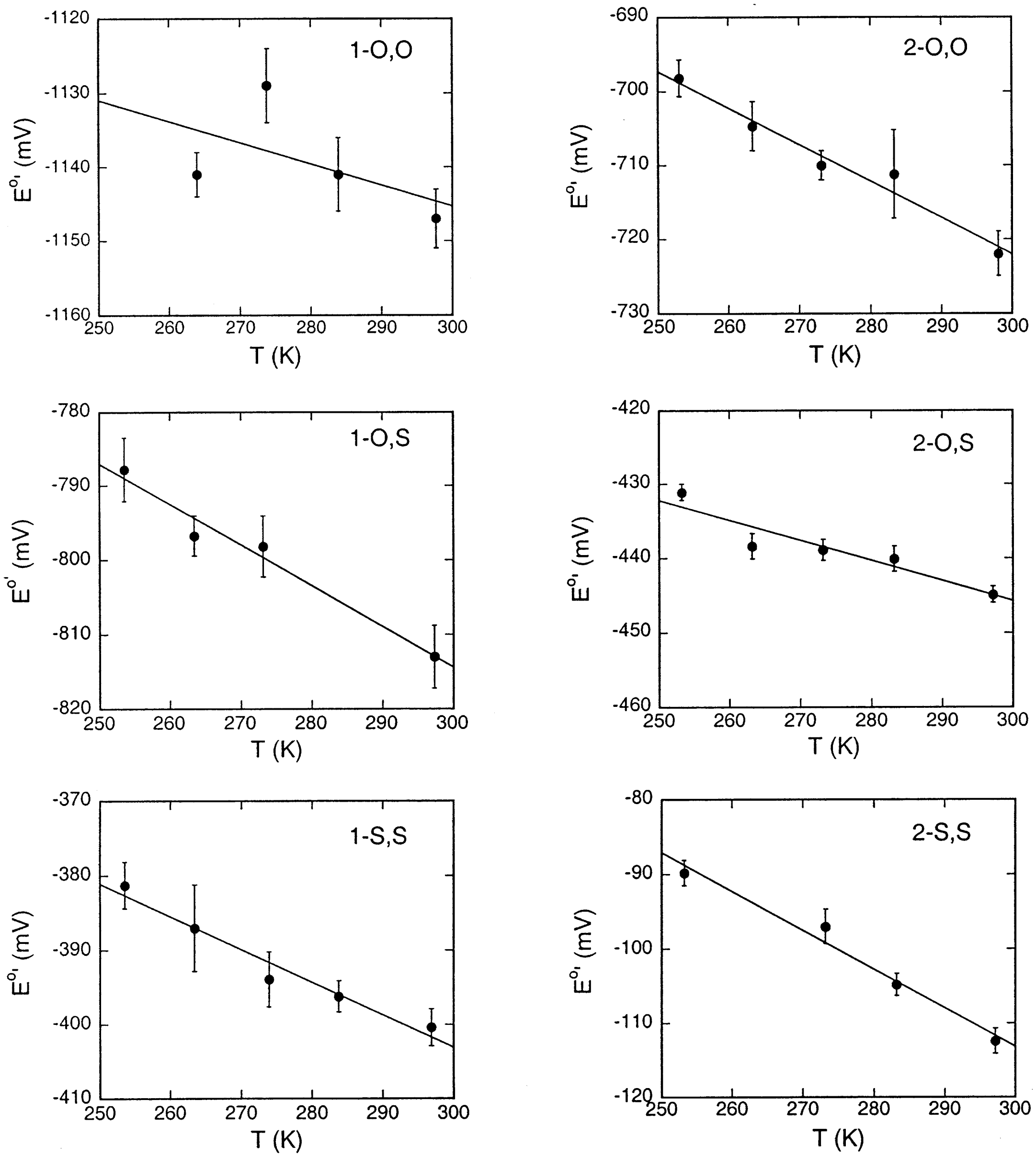

Figure 2. Plots of $E^{\circ\prime}$ versus T for [(Tp*)MoO(X,Y)]$^{0/-}$ couples in 0.3 M TBAPF$_6$/CH$_3$CN.

10-fold enhancement for compounds **2a**−**c**. Values of $E^{\circ\prime}$ and $k_{s,h}$ recorded at 297 K are reported in Table 1 and are in good agreement with results obtained in an earlier study of these compounds at ambient temperature.[7]

The temperature dependence of the thermodynamics of reaction 1 is illustrated in Figure 2. Values of the electrochemical half-reaction entropy, $\Delta S^{\circ}_{rc} = F(\partial E^{\circ\prime}/\partial T)$, obtained from the slopes of the $E^{\circ\prime}$ versus T plots are collected in Table 1. The quantities range from −26 to −53 J mol^{-1} K^{-1}. There is no discernible dependence of ΔS°_{rc} on ligand composition, and values are consistent with results anticipated for a 0/1− redox couple in CH$_3$CN in which no

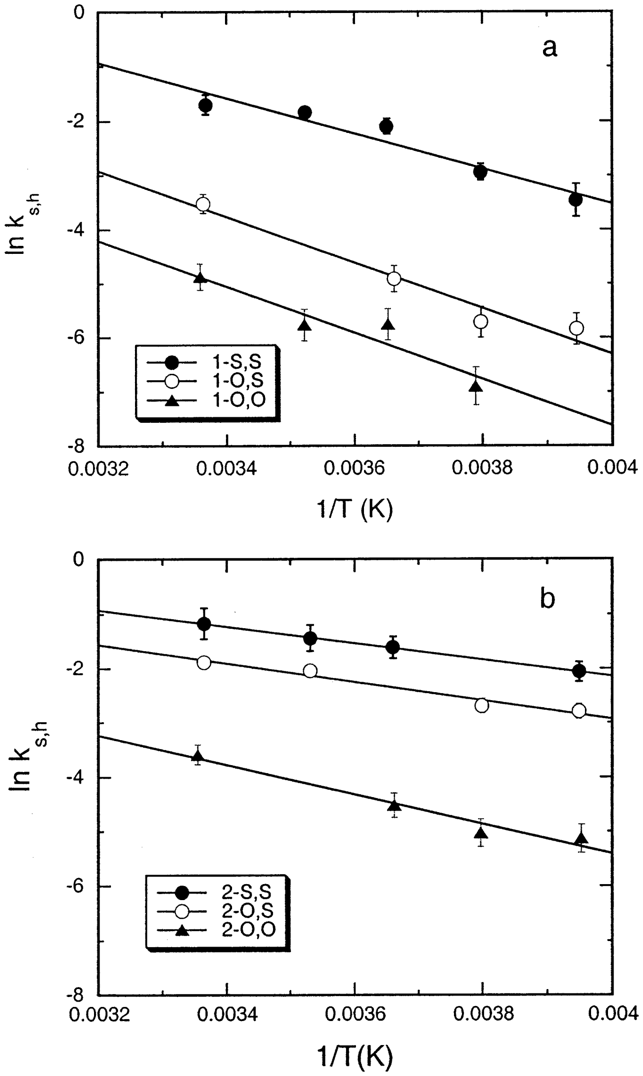

Figure 3. Temperature dependence of $k_{s,h}$ for (a) $[(Tp^*)MoO(1\text{-}X,Y)]^{0/-}$ and (b) $[(Tp^*)MoO(2\text{-}X,Y)]^{0/-}$ couples in 0.3 M $TBAPF_6/CH_3CN$.

compositional or large structural change accompanies electron transfer.[25] The large uncertainty in $\Delta S°_{rc}$ for compound **1a** is attributed to the large peak potential separations observed for this compound.

The temperature dependence of $k_{s,h}$ is illustrated in Figure 3. Values of $\Delta H^{\ddagger}$, ln A_{het}, and A_{het} determined from the slopes and intercepts of plots of ln $k_{s,h}$ versus $1/T$ as $\Delta H^{\ddagger} = -R\,\partial[\ln(k_{s,h})]/\partial(1/T)$, $\ln A_{het} = \ln(k_{s,h}) + \Delta H^{\ddagger}/RT$, and $A_{het} = k_{s,h}\cdot\exp[\Delta H^{\ddagger}/RT]$ are presented in Table 1. The results indicate that there are detectable influences of ligand composition on electrochemical activation parameters. Within each family of compounds, $\Delta H^{\ddagger}$ decreases by 9−10 kJ mol^{-1} on passing from ligands with two O donors to ones with two S donors. Moreover, values of $\Delta H^{\ddagger}$ are 13−21 kJ mol^{-1} larger for each compound in family **1a**−**c** than the corresponding member in sequence **2a**−**c**. Thus, compounds containing bidentate ligands with O donors and an aliphatic framework exhibit larger barrier heights.

Although there is considerable uncertainty in the experimental determination of the pre-exponential factor, the relative magnitudes of this quantity are informative. Values of A_{het} fall in the range 1.2−4.4 × 10^4 cm s^{-1} for compounds **1a**−**c** and 0.5−2.5 × 10^2 cm s^{-1} for compounds **2a**−**c**. These ranges are within ~1 order of magnitude of the result 3 × 10^3 cm s^{-1} calculated as $Z_{het} = (kT/2\pi m)^{1/2}$ for a 500 g mol^{-1} reactant. This is a typical value for the prefactor of a simple adiabatic electrode reaction in a nonaqueous solvent.[10b,21] It is evident from the data in Table 1 that A_{het} is not influenced by the change from O to S donor atoms in either series of compounds. However, complexes with aliphatic X,Y ligands exhibit a pre-exponential factor that is 50−200 times larger than that of the corresponding aromatic ones.

Discussion

Sulfur has a significant influence on the thermodynamics and kinetics of the $[(Tp^*)MoO(X,Y)]^{0/-}$ electrode reactions. The potential of $Mo^{V/IV}$ reduction shifts in the positive direction by ~0.3 V upon each systematic replacement of O by S. In addition, $E°'$ values are 0.3−0.4 V more positive for X,Y ligands with aromatic versus aliphatic frameworks. Similar effects have been observed in a number of instances,[28,29] but the results obtained in the current study are dramatic evidence of such behavior.

The influence of ligand structure and composition on metal-centered redox potentials frequently is explained in terms of an isolated orbital model, in which the energy of the redox active molecular orbital, here, the nonbonding Mo d_{xy}, increases or decreases in response to the amount of negative charge donated by the ligands.[30] Our present findings are consistent with this interpretation and the expectation within the context of hard and soft acid−base theory[31] that ligands with O versus S donors or aliphatic versus aromatic frameworks are more effective negative charge donors to an electropositive metal center. However, it is important to recognize that other factors contribute to thermodynamic stability. In a recent series of papers, Kennepohl and Solomon conducted a thorough analysis of electronic structure contributions to electron-transfer reactivity.[32−34] An important conclusion of their work is that the electronic relaxation, which accompanies valence ionization and electron attachment processes in metal−ligand complexes, makes an important contribution to redox thermodynamics. Relaxation involves a change in the repulsive

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interactions between metal-based electrons upon a change in oxidation state. The process is influenced by ligand composition and structure as well as metal−ligand covalency and operates in conjunction with orbital energy effects in modulating the charge density at a metal center and in determining the $E^{\circ\prime}$ value for a particular redox system. The magnitude of electronic relaxation is not known for compounds **1a**−**c** and **2a**−**c** but undoubtedly makes an important contribution to their relative $E^{\circ\prime}$ values.

Electrochemical activation parameters provide insight to the influence of ligand structure on electron-transfer kinetics. The activation enthalpies measured in this work equal the sum of inner- and outer-shell reorganizations that accompany the electrode reaction described by eq 1. To obtain an estimate of their inner-shell contributions, experimental values of $\Delta H^{\ddagger}$ are corrected by subtraction of an outer-shell component, $\Delta H^{\ddagger}_{os}$, which is calculated to equal 19 kJ mol^{-1} for compounds **1a**−**c** and 15 kJ mol^{-1} for compounds **2a**−**c** by use of the mean spherical approximation.[35]

$$\Delta H^{\ddagger}_{os} = Ne^2/8r[T(\partial\epsilon_{op}/\partial T)/\epsilon^2_{op} - (1 - 1/\epsilon_{op}) + \{(1 - 1/\epsilon_s) - T(\partial\epsilon_s/\partial T)/\epsilon^2_s\}/(1 + \delta_s/r) + T(1 - 1/\epsilon_s)(\partial\delta_s/\partial T)/r(1 + \delta_s/r)^2] \quad (5)$$

Here, ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, δ_s is the solvent polarization parameter, and r is the radius of the reactant. Values of $\Delta H^{\ddagger}_{is} = \Delta H^{\ddagger} - \Delta H^{\ddagger}_{os}$ are collected in Table 1. For compounds **2b** and **2c**, the outer-shell contribution equals the total barrier height within experimental error; thus, $\Delta H^{\ddagger}_{is}$ is effectively zero for these examples. However, there is a residual barrier height of 8 kJ mol^{-1} for compound **2a** (X,Y = 2-O,O). In a similar manner, the residual activation enthalpy for complex **1a**, which contains two O donors is 9 kJ mol^{-1} larger than that for complex **1c**, which contains two S donors. Also, $\Delta H^{\ddagger}_{is}$ is systematically 10 kJ mol^{-1} or more greater for all complexes with an aliphatic framework versus those with an aromatic framework.

Insufficient structural data are available for representative Mo^{V} and Mo^{IV} complexes to evaluate the influence of molecular structure on the experimental barrier heights in Table 1. However, the recent study of Kennepohl and Solomon includes a consideration of the influence of electronic relaxation on electron-transfer kinetics.[34] The results of their investigation provide a basis for qualitatively interpreting the differences in $\Delta H_{is}^{\ddagger}$. An importance kinetic consequence of electronic relaxation is that the bond-distorting forces and bond-distance changes, which comprise inner-shell reorganization, are relieved to various extents by the electronic charge redistribution that accompanies metal-centered oxidation or reduction. Because of their covalency, metal−thiolate bonds are particularly effective in this regard. However, the ameliorating effects of electronic relaxation do not occur as extensively in metal−alkoxide or metal−phenoxide complexes; hence, these systems will exhibit significantly larger inner-shell reorganization energies than their metal−thiolate analogues. A further consideration is that the entirety of each molecule is available to mediate redox-induced charge redistribution. Hence, an aromatic ligand framework should be more effective than an aliphatic one in this regard and exhibit smaller $\Delta H_{is}^{\ddagger}$ values. We conclude that the greater charge redistribution available via electronic relaxation to Mo−S and aromatic complexes in comparison to Mo−O and aliphatic ones is the principal mediator of $[(Tp^*)MoO(X,Y)]^{0/-}$ kinetics and is manifested experimentally in inner-shell reorganization barriers.[36,38] Thus, as is evident from the data in Table 1, enthalpic effects are the primary determinant of the electron-transfer rate differences among the compounds investigated.

Pre-exponential factors were measured in an attempt to assess the influence of donor atom character on the adiabaticity of reaction 1. It was anticipated that relative values of A_{het} might point to instances of poor electronic coupling between the electrode and the Mo-centered redox orbital, which could be taken as evidence that $\kappa_{el} < 1$.[39] However, the results in Table 1 show no systematic correlation between the pre-exponential factor and the O or S content of the ligands. Therefore, although Mo−S orbital overlap may be effective in modulating metal−ligand covalency and various physical and chemical properties of molybdenum enzyme model systems,[3−6] it apparently is without effect on the adiabaticity of Mo-centered electron transfer in these electrochemical reactions. On the other hand, we do observe a measurable influence of aromatic versus aliphatic ligand character on the experimentally observed prefactor. The origin of this difference is not understood, although the following rationalizations have been considered. One is based on the report of Kennepohl and Solomon that electronic relaxation decreases electronic coupling.[34] However, the effect is small (∼20%) and should be influenced by S content as well as ligand framework. A second possibility follows from the recent study of Compton et al., which correlates the electrochemical rate constants of a series of anthracene derivatives with their molecular size.[40] Qualitatively, the behavior reflects the effectiveness of the reactant in approaching the electrode surface and can be incorporated as an additional term in the pre-exponential factor of eq 3. Our

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(35) Fawcett, W. R.; Blum, L. *Chem. Phys. Lett.* **1991**, *187*, 173.

(36) On the basis of a simple harmonic oscillator model of inner-shell reorganization, $\Delta H^{\ddagger}_{is} = 1/2 \cdot \Sigma f(\Delta a/2)^2$ (ref 16), and force constants of $f = 300$ and 150 N m^{-1} for Mo−O and Mo−S single bonds (ref 37), respectively, it is calculated that bond-length displacements of $\Delta a \approx 20$ pm must occur to account for the ∼10 kJ mol^{-1} difference in $\Delta H^{\ddagger}_{is}$ between the O,O and S,S entries in Table 1, if reorganization is limited to the bonds between Mo and the donor atoms of the bidentate X,Y ligand. This value seems large for electron-transfer involving an effectively nonbonding Mo d_{xy} orbital, which speaks against a highly localized model of inner-shell reorganization.

(37) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(38) We also have noted similarly large differences in $E^{\circ\prime}$ and $k_{s,h}$ for two-electron transfer in sulfido- vs phosphido-bridged metal carbonyl dimers, $[M_2(\mu\text{-SPh})_2(CO)_8]^{0/2-}$ and $[M_2(\mu\text{-PPh}_2)_2(CO)_8]^{0/2-}$ (M = Mo, W), and surmise that a parallel explanation may apply in this case: Uhrhammer, D.; Schultz, F. A. *J. Phys. Chem. A* **2002**, *106*, 11630.

(39) This conclusion also rests on the generally held assumption that the intrinsic activation entropy of a simple adiabatic electrode reaction ($\Delta S^{\ddagger}$ in eq 3) is near zero (ref 16b).

(40) Clegg, A. D.; Rees, N. V.; Klymenko, O. V.; Coles, B. A.; Compton, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 6185.

results are consistent with the explanation of Compton in that (beyond a limiting small size) smaller reactants produce a larger pre-exponential term. However, only a factor of 2−4 can be accounted for on the basis of the analysis in ref 40 and the hydrodynamic radii of our reactants, which is small in comparison to the experimentally observed factor of 50−200. Thus, further investigation is needed to account for the observed differences in A_{het}.

Conclusion

The presence of sulfur versus oxygen donors and an aromatic versus aliphatic framework in bidentate 1,2-disubstituted X,Y ligands shifts $E^{\circ\prime}$ in the positive direction and increases the electrochemical electron-transfer rate constant for $\mathrm{Mo^{V/IV}}$ reduction in $(\mathrm{Tp^*})\mathrm{Mo^VO(X,Y)}$ complexes. These observations are attributed to more effective charge redistribution via electronic relaxation throughout the entire molecular structure for S versus O and aromatic versus aliphatic systems. Temperature-dependent measurements of $k_{\mathrm{s,h}}$ indicate that differences in the electron-transfer rate constant arise primarily from differences in the inner-shell enthalpy of activation. There is no indication that sulfur donors or an aromatic ligand framework are more effective than their structural counterparts in enhancing electronic coupling between the electrode and the Mo d_{xy} redox orbital.

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Supporting Information Available: Tables of electrochemical data as a function of temperature and plots of corrected peak potential separations as a function of scan rate at 297 K for compounds **1a**−**c** and **2a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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