Thermodynamics, Kinetics, and Mechanism of the Reversible Formation of Oxorhenium(VII) Catecholate Complexes

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Mononuclear Re(V) compounds MeReO(mtp)NC$_5$H$_4$X, **3**, where mtpH$_2$ is 2-(mercaptomethyl)thiophenol have been prepared from the monomerization of {MeReO(mtp)}$_2$ by pyridines with electron-donating substituents in the para or meta position; X = 4-Me, 4-Bu^t, 3-Me, 4-Ph, and H. Analogous compounds, MeReO(edt)N$_5$H$_4$X, **4**, edtH$_2$ = 1,2-ethanedithiol, were prepared similarly. The equilibrium constants for the reaction, dimer + 2Py = 2M−Py, are in the range (2.5−31.6) × 10^2 L mol^{-1}. Both groups of monomeric compounds react with quinones (phenanthrenequinone, PQ, and 3,5-*tert*-butyl-1,2-benzoquinone, DBQ), displacing the pyridine ligand and forming Re(VII) catecholate complexes MeReO(dithiolate)PCat and MeReO(dithiolate)DBCat. With PQ, the reaction MeReO(dithiolate)Py + PQ = MeReO(dithiolate)PCat + Py is an equilibrium; values of K_Q for different Py ligands lie in the ranges 9.2−42.7 (mtp) and 3.2−11.2 (edt) at 298 K. These second-order rate constants (L mol^{-1} s^{-1}) at 25 °C in benzene were obtained for the PQ reactions: k_f = (5.3−15.5) × 10^{-2} (mtp), (6.6−16.4) × 10^{-2} (edt); k_r = (3.63−5.71) × 10^{-3} (mtp), (14.7−22.0) × 10^{-3} (edt). The ranges in each case refer to the series of pyridine ligands, the forward rate constant being the largest for C$_5$H$_5$N, with the lowest Lewis basicity. The reactions of MeReO(dithiolate)Py with DBQ proceed to completion. Values of k_f/L mol^{-1} s^{-1} fall in a narrow range, 4.02 (X = Bu^t) to 8.4 (X = H) with the dithiolate being mtp.

Introduction

The chemistry of Re(VII) complexes with strongly π-donating oxygen and nitrogen ligands has been of considerable recent interest. One particular compound that has been studied extensively is methyltrioxorhenium(VII) (MeReO$_3$ or MTO). Condensation reactions provide a means of derivatizing metal−oxo groups:

$$M{=}O + H_2Y \text{ (or 2HZ)} \rightarrow H_2O + MY \text{ (or } MZ_2\text{)} \qquad (1)$$

We have previously used this type of reaction to convert MTO into a dimeric dithiolato−Re(V) complex **1** by reaction with dithiols:[1,2]

$$2MeReO_3 + 4mtpH_2 \rightarrow \{MeReO(mtp)\}_2 + 2RS{-}SR + 4H_2O \qquad (2)$$

Here mtpH$_2$ is 2-(mercaptomethyl)thiophenol and RS−SR its oxidation product, the cyclic disulfide. The dimer {MeReO(edt)}$_2$, **2** (edtH$_2$ = ethane-1,2-dithiol), is formed from Me$_2$Re$_2$O$_2$(SPh)$_4$, edtH$_2$ and dimethyl sulfide.[3] These compounds and their mononuclear counterparts formed by ligand (e.g., pyridine) addition to the dimers, MeReO(mtp)Py and MeReO(edt)Py, are proving to be effective catalysts for oxygen transfer reactions.[3−5] Two factors are important. One is the Re(V)−Re(VII) transformation by O-atom uptake, and its reverse, these steps being the ones that accomplish oxygen transfer. The second factor concerns the rates and mechanism of ligand substitution.[6,7] The reaction between oxorhenium(V) compounds and *ortho*-quinones addresses both of these issues while avoiding the complication of net oxygen-atom transfer.

Quinones and catechols are of considerable biological significance. Enterobactin, for example, is a siderophore consisting of three *ortho*-catecholate groups.[8] Catecholamines such as epinephrine, norepinephrin, and dopamine are *ortho*-catechols that are used as neurotransmitters.[9] Catecholate complexes of oxotechnetium(V) have been studied as models for synthetic precursors to radiopharmaceutical proteins,[10−16] and thus ^{99m}Tc and ^{186}Re catecholates hold potential interest in nuclear medicine.[16]

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Several high-valent rhenium catecholate complexes have been identified. The Re(V) compounds include $[ReO(Cat)(PPh_3)_2X]$ (X = Cl, I),[17] $ReO(Cat)_2(OPPh_3)]^-$,[17] $[ReO(Cat)_2(PPh_3)_2]^-$,[16] and $[Cp^*Re(Cat)_2]$.[18] There is even one compound, $\{ReO[O(OH)C_6H_4](S_2CNEt_2)_2\}$, in which the catecholate binds in a monodentate fashion.[19] The dark purple compound $Re(DBCat)_3$ is a rare example of a Re(VI) compound stable to air and water.[20,21] The crystal structure of $[Me_4N][ReO_2(Cat)_2]$ was determined.[22] Chelated rhenium−semiquinone complexes do exist but only when rhenium is in a low oxidation state such as $Re(CO)_4(DBSQ)$.[23]

The condensation reaction between MTO and catechol forms $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(NC_5H_5)$.[24] A second compound, $CH_3Re(O)_2(9,10\text{-}O_2C_{14}H_8)(NC_5H_5)$, was prepared by the oxidation of $MeReO_2$, obtained in-situ from MTO and polymer-supported PPh_3, with phenantherenequinone. In effect, the condensation reaction between Re(VII) and catechol ($CatH_2$, meant to include ring-substituted 1,2-dihydroxyarenes in general) affords one route to $MeReO_2(1,2\text{-}Cat)$.[24] Oxidation of Re(V) by quinones forms the same material.[24] The net reactions are the following:

$$MeReO_3 + CatH_2 \rightleftarrows MeRe(O)_2(Cat) + H_2O \qquad (3a)$$

$$MeReO_2 + Quin \rightleftarrows MeRe(O)_2(Cat) \qquad (3b)$$

The products are best regarded as catecholate complexes of Re(VII). They are intensely colored species, shades of deep blue and violet depending on the substituents.[25] The spectroscopic characteristics undoubtedly arise from low-energy, allowed LMCT transitions. As indicated, these reactions are reversible. They proceed at measurable rates in aqueous and semiaqueous media to extents that depend on the identity of the catechol and particularly on the activity of water.[25]

To limit the number of variables we did not use $MeReO_2$ as the reagent but instead chose related Re(V) compounds with a single oxorhenium group. We have thus studied the reactions of a series of mononuclear methyl(oxo)rhenium(V) compounds with quinones. In addition to the methyl and oxo groups, they contain a chelated dithiolate ligand, mtp or edt, and one other ligand, usually pyridine. They are rhenium(V) compounds, MeReO(mtp)Py (**3**) and MeReO(edt)Py (**4**), prepared by pyridine addition to dimer **1** (or **2**) formed according to the equilibrium

$$\{MeReO(dithiolate)\}_2 + 2Py \rightleftarrows 2MeReO(dithiolate)Py \quad K_1 \quad (4)$$

The structural formulas of the participants are given in Chart 1. The structures of **1** and **3** have been established by single-crystal X-ray diffraction,[1] as has the PPh_3 analogue of **4**.[26] Upon reaction with quinone, pyridine is displaced in a reversible reaction,

$$MeRe^{V}O(dithiolate)Py + Q \rightleftarrows MeRe^{VII}O(dithiolate)Cat + Py \quad K_Q \quad (5)$$

Table 1. Equilibrium Constants for Monomerization (K_1, Eq 4) and Quinone/Catecholate ($K_{Q,}$ Eq 5) Reactions

	MeReO(mtp)−Py		MeReO(edt)−Py	
Py	$K_1/10^3$ L mol^{-1} [a,b]	K_Q[c]	$K_1/10^3$ L mol^{-1} [a]	K_Q[c]
4-Bu^t-C_5H_4N	4.07	9.2(3)	3.16(7)	3.2(2)
4-Me-C_5H_4N	1.00	12.0(5)	2.24(5)	3.5(2)
3-Me-C_5H_4N	1.07	22.6(6)	1.26(3)	5.0(2)
4-Ph-C_5H_4N	1.15	21.7(6)	0.98(2)	5(1)
C_5H_5N	0.174	42.7(7)	0.25(1)	11.2(4)

[a] For reaction 4. [b] From ref 7. [c] For reaction 5.

The thermodynamics and kinetics of these reactions have not been studied previously, neither for Re(VII) with catechol nor Re(V) with quinone. Two dithiolates were used in the course of this research, mtp and edt (Chart 1) and two quinones, phenanthrenequinone (PQ) and 3,5-di-*tert*-butylbenzoquinone (DBQ), each with one of five pyridine ligands. These reactions do not attain completion but reach an equilibrium position dependent on the particular reagents used and their concentrations. The objectives of this research have been to characterize the kinetics, identify the steps that comprise the mechanism, and evaluate their rates and equilibrium constants.

Experimental Section

Materials. Benzene (Fisher spectranalyzed) was used as the solvent for all UV−vis kinetic studies. The solvent utilized for NMR studies was deuterated benzene (Cambridge Isotope Laboratories). Dimer **1** was prepared as described in the literature,[1] and dimer **2** was synthesized from $Me_2Re_2O_2(SPh)_4$, $edtH_2$ and dimethyl sulfide.[3] Pyridine (Fisher) was used as received. Other reagents, including 1,2-phenanthrenequinone, 3,5-di-*tert*-butyl-1,2-benzoquinone, and ring-substituted pyridines, were purchased from Aldrich and used as received.

Instrumentation. UV−visible kinetic studies were carried out with the use of Shimadzu scanning spectrophotometers equipped with electronic temperature controlled cell holders. A Shimadzu diode-array spectrophotometer was used for rapid, repetitive spectral scans. ^1H NMR spectra were acquired with the use of Bruker DRX-400 or Varian VXR-400 spectrometers. The ^1H chemical shifts were referenced to the residual proton resonance of the deuterated benzene, $\delta = 7.16$ ppm.

Results

Equilibrium Constants. The equilibrium constants (K_1) for the monomerization reaction (eq 4) between $\{MeReO(mtp)\}_2$ and five ring-substituted pyridines are available in the literature[6] and are given in Table 1. The values of K_1 for the previously unexplored compound $\{MeReO(edt)\}_2$ were determined from the spectra of solutions of this dimer in equilibrium with each of five pyridines, generically designated Py. The program PSEQUAD[27] was used to determine K_1 by a global fit of absorbance−concentration data taken at 22 wavelengths in the range 400−620 nm. The concentrations were 0.8 mM Re_T and

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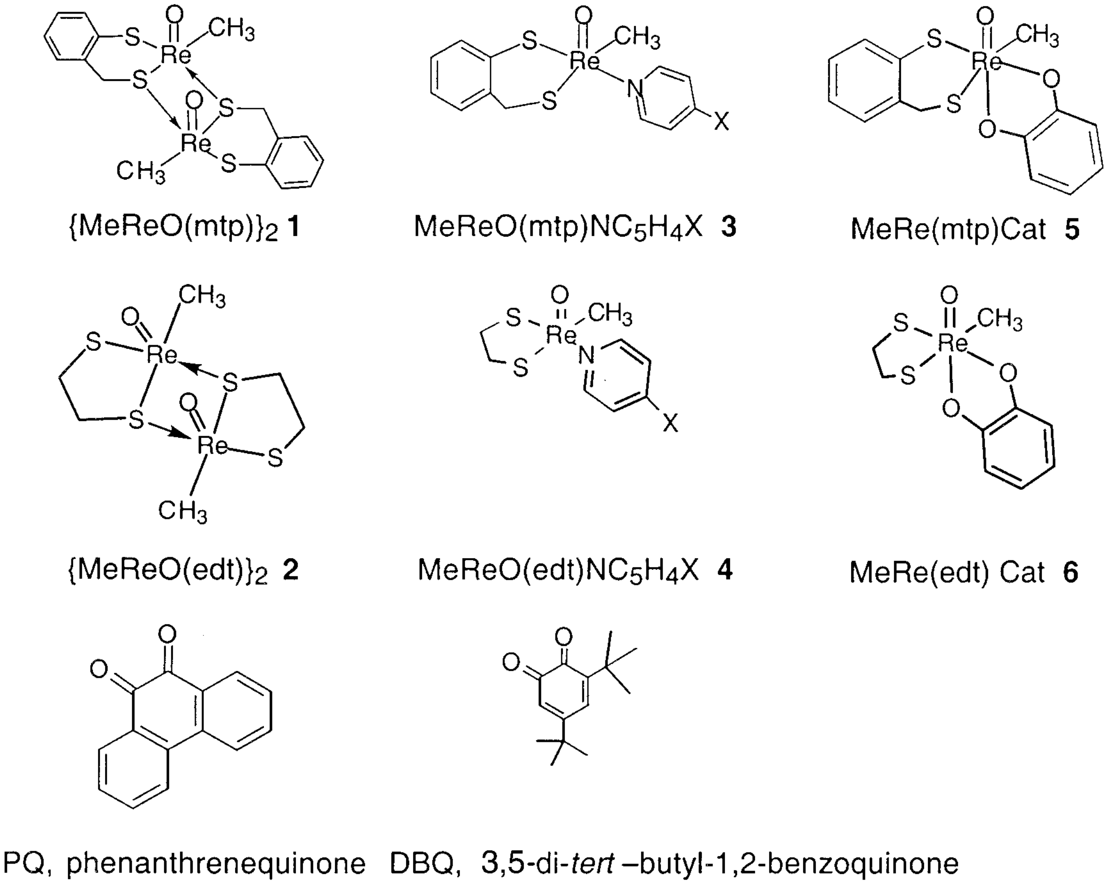
Chart 1. Structural Formulas for Participating Compounds, with Quinone and Catechol Shown Generically


{MeReO(mtp)}$_2$ **1**

MeReO(mtp)NC$_5$H$_4$X **3**

MeRe(mtp)Cat **5**

{MeReO(edt)}$_2$ **2**

MeReO(edt)NC$_5$H$_4$X **4**

MeRe(edt) Cat **6**

PQ, phenanthrenequinone DBQ, 3,5-di-*tert*-butyl-1,2-benzoquinone

Table 2. Visible and ^{1}H NMR Spectra of MeRe^{VII}O(dithiolate)Cat[a] and MeRe^{V}(dithiolate)Py Complexes

	λ_{max}/nm (ϵ/10^3 L mol^{-1} cm^{-1})[b]		^{1}H NMR, Re−CH_3 δ[c,d]	
compd	mtp	edt	mtp	edt
MeReO(dithiolate)Py	608 (0.255)	545 (0.234)	2.77 (s)[e]	2.46 (s)
MeReO(dithiolate)PCat	595 (15.9)	581 (13.7)	1.85 (s)	2.18 (s)
MeReO(dithiolate)DBCat	550 (17.0)	531 (10.7)	1.74, 1.77[f]	2.47, 2.70[f]

[a] PQ = phenanthrenequinone; DBQ = 3,5-di-*tert*-butylbenzoquinone. [b] For PQ, from extrapolation of the spectrum to high [M-Py]; for DBQ, from the measured absorbances. [c] In C$_6$D$_6$. [d] The chemical shifts for the CH$_2$ groups of dithiolate ligands are the following: MeReO(mtp)PCat, δ 5.23 (d, 1H), 5.48 (d, 1H); MeReO(edt)PCat, 3.56 (m, 2H), 4.08 (m, 1H), 4.18 (m, 1H); MeReO(edt)Py, 2.76 (br, 2H), 3.25 (br, 1H), 4.01 (br, 1H); MeReO(mtp)DBCat (two isomers), 5.06 (d, 1H), 5.19 (d, 1H), 5.44 (m, 2H); MeReO(edt)DBCat (two isomers), 3.22 (m, 2H), 3.66 (m, 2H), 3.83 (m, 2H), 4.17 (m, 1H), 4.28 (m, 1H). [e] Reference 7. [f] Two isomers are present; see text.

0.5−41 mM Py. The values of K_1 so calculated are given in Table 1. The values of K_1 for the mtp and edt complexes do not differ greatly.

The reactions of MeReO(dithiolate)Py (or **M**−Py) complexes with quinones are accompanied by large absorbance increases, signaling the formation of the intensely absorbing product MeReO(dithiolate)Cat. The equilibrium constants (K_Q) for those reactions were determined directly from the equilibrium absorbances. These experiments were carried out with [PQ] ≪ [**M**−Py]. The equilibrium absorbance/cm of optical path is given by

$$\mathrm{Abs} = \epsilon_{\mathrm{M-Py}}[\mathbf{M}\mathrm{-Py}] + \epsilon_{\mathrm{M-Cat}}\left(\frac{K_Q\dfrac{[\mathbf{M}\mathrm{-Py}]}{[\mathrm{Py}]}}{1 + K_Q\dfrac{[\mathbf{M}\mathrm{-Py}]}{[\mathrm{Py}]}}\right)[\mathrm{PQ}]_T \quad (6)$$

The values of the equilibrium constants, K_Q, determined by least-squares fitting are given in Table 1. The absorption maximum and molar absorptivity of each **M**−Cat species are summarized in Table 2. An example of that is given in the Supporting Information, Figure S-1. The reactions of DBQ proceeded to completion at all the concentrations used, allowing the spectrum of the product to be determined by direct measurement.

Kinetics. Spectrophotometric methods were used throughout, following the buildup of the product. A typical repetitive scan experiment is shown in Figure 1. These determinations were conducted principally at the absorption maximum with occasional checks at other wavelengths.

The kinetic data for the PQ reactions were analyzed by reversible kinetics, according to the rate equation

$$-\frac{d[\mathbf{M}\mathrm{-Py}]}{dt} = \frac{d[\mathbf{M}\mathrm{-PCat}]}{dt} = k_f[\mathbf{M}\mathrm{-Py}][\mathrm{PQ}] - k_r[\mathbf{M}\mathrm{-PCat}][\mathrm{Py}] \quad (7)$$

With MeReO(mtp)Py at concentrations much higher than those of the other species, the approach to equilibrium follows pseudo-

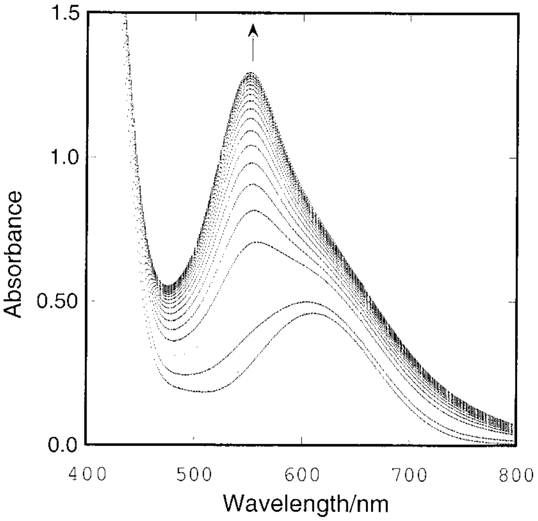


Figure 1. Repetitive scans in a 1-cm cuvette of the visible spectrum during a reaction between 2.0 mM MeReO(mtp)Py and 60 μM DBQ in the presence of 18 mM Py in benzene at 25.0 °C. The interval between scans was 12 s, except for the first two spectra, where it was 5 s.

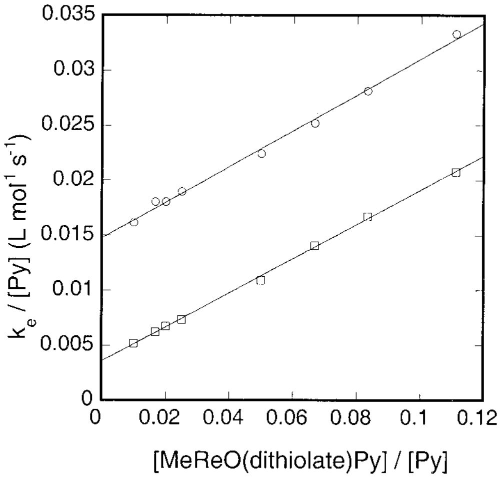


Figure 2. Analysis of the kinetic data for the equilibration kinetics for the reactions of MeReO(dithiolate)Py with PQ, by plots of k_e/[Py] against [MeReO(dithiolate)Py]/[Py] according to eq 9. Values are shown for dithiolate = mtp (squares) and edt (circles) pertaining to experiments in benzene at 25.0 °C. The error bars of the fits lie within the symbols; actual errors between experiments are of the order of 2%, largely from imprecision in concentrations.

first-order kinetics. The rate constant for equilibration is given by

$$k_e = k_f[\mathbf{M}-\mathrm{Py}] + k_r[\mathrm{Py}] \qquad (8)$$

One method of exploring the fit to this equation is provided by this rearranged equation,

$$\frac{k_e}{[\mathrm{Py}]} = k_r + k_f\frac{[\mathbf{M}-\mathrm{Py}]}{[\mathrm{Py}]} \qquad (9)$$

Figure 2 displays the data for MeReO(mtp)Py and MeReO(edt)Py against the indicated concentration ratio. The data are indeed linear, confirming this model. The intercept affords k_r from the intercept and k_f from the slope. Values of the rate constants that are more meaningful statistically can be obtained by direct fits to eq 7 using a program that accommodates two x-variables.[28] The rate constants obtained by the latter method are given in Table 3. The kinetic data for the DBQ reactions, which proceeded to completion, were fit to first-order kinetics. The values of the pseudo-first-order rate constants (k_ψ) were determined as a function of [MeReO(mtp)Py], the concentration of which was chosen to be $\gg$[DBQ]. As shown in Figure S-2 in the Supporting Information, k_ψ varies linearly with [**M**−Py] and the line extrapolates to the origin. These rate constants are k_5 = 4.02(5) L mol^{-1} s^{-1} for 4-Bu^{t}C$_5$H$_5$N and 8.4(1) L mol^{-1} s^{-1} for C$_5$H$_5$N.

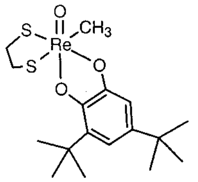
Table 3. Rate Constants for the Forward and Reverse Steps of the Reactions between MeReO(dithiolate)−Pyridine and Phenanthrenequinone[a]

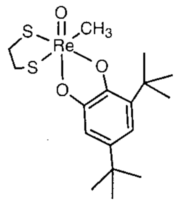
	k_f/10^{-2} L mol^{-1} s^{-1}		k_r/10^{-3} L mol^{-1} s^{-1}	
pyridine	mtp	edt	mtp	edt
4-Bu^{t}C$_5$H$_4$N	5.3(1)	6.6(4)	5.71(6)	20.6(2)
4-MeC$_5$H$_4$H	6.5(2)	7.7(5)	5.4(1)	22.0(2)
3-MeC$_5$H$_4$N	9.1(2)	7.7(2)	4.01(6)	15.4(1)
4-PhC$_5$H$_4$N	9.4(2)	11(3)	4.36(6)	21(1)
C$_5$H$_5$N	15.5(1)	16.4(5)	3.63(5)	14.7(2)

[a] In benzene at 25.0 °C.

We attempted to shift the equilibrium position of **M**−DBCat systems back to the left (eq 5) by diluting with solvent simultaneously with all the components other than Py, to evaluate the equilibrium constant and the reverse rate constant more directly. This was not successful, as the decomposition of MeReO(mtp)DBCat interfered. Insofar as we could determine, the reaction of DBQ proceeds entirely to completion.

The ^{1}H NMR spectra for the complexes derived from 3,5-di-*tert*-butyl-1,2-benzoquinone, which are presented in Table 2, indicate the presence of two stereoisomers, as shown here





for edt, and likewise for mtp. There is little difference between them, and it is not surprising that the two are formed in nearly the same amount. This means that the rate constant is the sum of two nearly identical rate constants for each isomer.

Activation Parameters. Rate constants for the forward and reverse directions of reaction 5 with "Py" = 4-Bu^{t}C$_5$H$_4$N and "dithiolate" = mtp were evaluated as a function of temperature over the range 288−333 K. The data were analyzed according to the transition-state theory equation,

$$\frac{k}{T} = \frac{k_B}{h}e^{(\Delta S^\ddagger/R)}e^{(-\Delta H^\ddagger/RT)} \qquad (10)$$

The activation parameters are the following:

	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
MeReO(mtp)NC$_5$H$_4$-4-Bu^t + PQ	53(2)	92(6)
MeReO(mtp)PCat + 4-Bu^{t}C$_5$H$_4$N	62(3)	82(6)

Reactions of the Re Dimers with Quinones. A reaction occurred between {MeReO(mtp)}$_2$ and PQ, as evidenced by the very slow increase in absorbance at 595 nm, consistent with the formation of MeReO(mtp)PCat. This occurred quite slowly

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(28) Scientist, 2.0 2.0, Micromath Software, 1995.

in comparison with reaction 5. The same reaction was then explored by adding 60 μM pyridine to the other two reagents. This led to a considerable increase in the rate of product formation, as shown in Figure S-3. The catalytic effect of Py can be attributed to the occurrence of reactions 4 and 5 in succession.

Reactions of Phosphines. Two types of experiments were carried out. In the first, MeReO(mtp)PPh_3 and an *ortho*-quinone (in this case, 1,2-naphthoquinone) were mixed. No rhenium catecholate was observed. It is known that the values of K_1 for phosphine ligands are much larger than those for pyridines, so much so that K_1 values could not be determined for phosphines.[6] Further, the values of the equilibrium constants K_Q for quinone reactions are not large numbers, Table 1. These two facts combine to indicate that it is not at all surprising to find that no reaction occurred between the phosphine complex and the quinone.

A second experiment involved the attempt to react the first-formed catecholate, MeReO(mtp)Pcat, with triphenylphosphine, reasoning that the strongly coordinating phosphine should release free quinone:

$$\mathrm{MeReO(mtp)PCat} + \mathrm{PPh_3} \rightarrow \mathrm{PQ} + \mathrm{MeReO(mtp)(PPh_3)} \tag{11}$$

The spectrum of the rhenium catecholate complex was indeed slowly bleached after phosphine was added. This bleaching could be the result of two different independent or simultaneous reactions. One is that shown in eq 11, and the other is that between PPh_3 and **M**−Py. This situation proved to be quite complex and not informative as to the matter being explored; it was not pursued further.

Other Diones. Mixing MeReO(mtp)NC_5H_4-3-Me with 2-methyl-1,4-naphthoquinone gave no evidence of formation of a rhenium complex. This is not surprising because a chelating catecholate cannot form; it does establish, however, that simple coordination is not a proper description of the reactions of the *ortho*-quinones.

Along the same line, an experiment was carried out with 1,2-cyclohexanedione and MeReO(mtp)Py in C_6D_6. The green color of the parent compound remained unchanged, as did its NMR spectrum even after 2 days.

Discussion

Spectra of MeReO(dithiolate)Py and MeReO(dithiolate)-Cat Complexes. The visible spectra (Table 2) of the **M**−Py complexes are characterized by a d−d band at λ_{max} 545 (edt) and 608 (mtp) nm, with respective molar absorptivities 234−255 L mol^{-1} cm^{-1}. The band lies at higher energy for MeReO(edt)Py as compared to MeReO(mtp)Py because the edt ligand is more electron-donating than mtp. The MeReO(dithiolate)-Cat complexes exhibit absorption maxima in the same wavelength region, but the molar absorptivities are nearly 2 orders of magnitude larger. Their intensity indicates that they are MLCT bands, arising from the donation of ligand electron density into the d-orbitals of the metal.

Equilibrium Constant of Monomerization Reactions. The values of K_1 (Table 1) for the reaction in which {MeReO(dithiolate)}$_2$ reacts with a pyridine ligand decrease as the electron-donating ability of that ligand decreases. From the present work, the range of the K_1 values for the edt complex is 0.25×10^3 (Py) to 3.2×10^3 (4-Bu^{t}C$_5$H$_4$). This study was limited to pyridine and those of its derivatives that are stronger Lewis bases, to avoid the intrusion of the parent dimer into the reaction of **M**−Py complexes with the quinones.

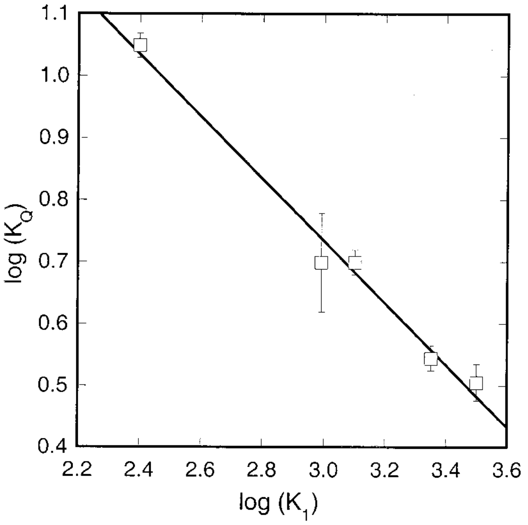


Figure 3. Comparison of the equilibrium constant for monomerization of {MeReO(edt)}$_2$, K_1, with that for the formation of MeReO(edt)-PCat, K_Q. The slope is -0.50 ± 0.04, conforming to the thermodynamic requirement.

Equilibrium Constant for Quinone Reactions. The reaction referred to is written in eq 5, and its equilibrium constant is designated as K_Q. The values of K_Q are >1, with a magnitude that increases as the Py ligand becomes less electron-donating. For example, for MeReO(edt)Py, the values of K_Q range from 3.2 (4-Bu^{t}C$_5$H$_4$N) to 11.2 (C_5H_5N). These values, and the trend they display, reflect the rate constants for the forward and reverse directions, as presented subsequently.

Comparison of K_1 and K_Q. There is a thermodynamically specified relation between the values of K_1 and K_Q. They are related by the chemical equation obtained by adding half of eq 4 to eq 5:

$$\frac{1}{2}\{\mathrm{MeReO(dithiolate)}\}_2 + \mathrm{Q} \rightleftarrows \mathrm{MeReO(dithiolate)Cat} \quad K_c \tag{12}$$

The relationship between the three equilibrium constants is thus

$$K_c = K_1^{1/2} K_Q \tag{13}$$

which can also be written

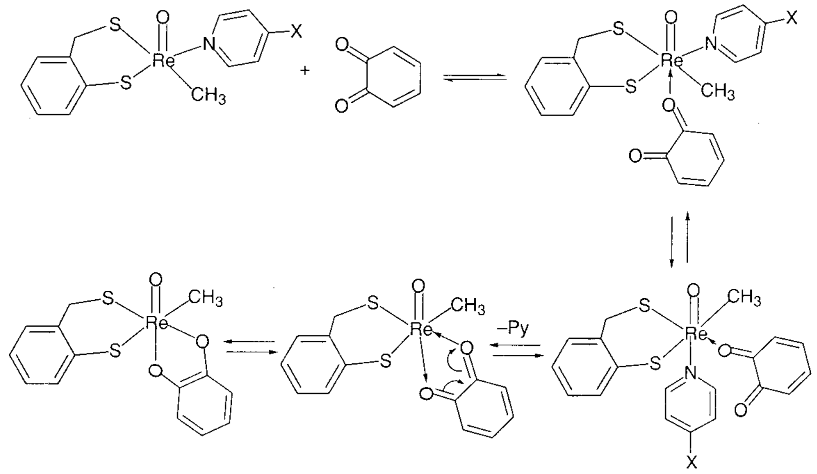
$$\log K_Q = \log K_c - \frac{1}{2}\log K_1 \tag{14}$$

The internal consistency of these data have been confirmed, and thus the model validated, by the linear plot of log K_Q against log K_1 presented in Figure 3, with a slope of −0.5 and an intercept that affords the value of log K_c.

Kinetics of the Reaction of MeReO(dithiolate)Py with PQ. As the pyridine becomes a weaker Lewis base, the forward rate constant increases by a factor of about 3 whereas the reverse rate constant decreases only slightly; see Table 3. The forward rate constant, for PQ addition, varies mildly among the Py ligands being displaced. (1) All variations are mild: a factor of about 3 encompasses the value. (2) The most weakly held pyridine is the one most readily displaced by PQ.

Comparisons between mtp and edt Complexes. The rate constants for the reactions of PQ with MeReO(mtp)Py and MeReO(edt)Py, for a given pyridine, are roughly the same. In

Scheme 1



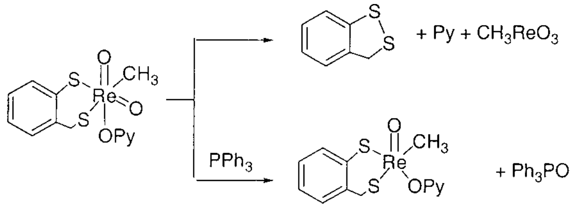
the reverse direction, however, the edt complex is about four times more reactive. Thus the reverse reaction depends on the characteristics of the ancillary dithiolate ligand. The edt is the more electron-donating of the two; it therefore releases the catechelato oxygen more readily, allowing the pyridine to reenter.

Kinetics of the Reaction between MeReO(mtp)Py and DBQ. This reaction proceeds to completion, and the reverse rate constant cannot be determined. Moreover, the forward rate constant is 50-fold greater than that for PQ, consistent with DBQ being much more electron-donating. Clearly, the forward rate constant depends strongly on the characteristics of the entering ligand.

Activation Parameters. The negative values of $\Delta S^{\ddagger}$ are probably reflective of little more than these being second-order reactions in which the diffusion and orientation of the pair of solute molecules dominates. We later propose the intervention of a reaction intermediate whose formation requires substantial organization. Indeed, the entropic barrier is substantial, $T\Delta S^{\ddagger}$ being roughly 26 kJ, about half the barrier from $\Delta H^{\ddagger}$.

Proposed Mechanism. The experimental data show the effects of entering PQ and DBQ, which are quite substantial. The rate constant is larger for DBQ by a factor of 76 ($\mathrm{Bu^tC_5H_4N}$) or 54 ($\mathrm{C_5H_5N}$). For a given quinone, the effect of changing from $\mathrm{Bu^tC_5H_4N}$ to $\mathrm{C_5H_5N}$ is minimal: a factor of 2.1 (DBQ) to 2.9 (PQ). These trends signal an associative mechanism, with major involvement of Re−O bond-making in the transition state and relatively little Re−Py bond-breaking. The reaction can be described as shown in Scheme 1. In the first step, the quinone approaches the vacant coordination site on the Re(V) reagent, interacting weakly with it. This generates an intermediate in which there is weak coordination of the quinone. The suggestion of a six-coordinate rhenium intermediate is supported by the recent preparation of MeReO(edt)(2,2′-bpy).[29] This intermediate undergoes a "turnstile" rotation,[30−34] placing the Py ligand trans to the oxo group. The turnstile mechanism has been proposed to explain the kinetics of monodentate ligand substitution reaction of the Re(V) complexes.[35] The trans-influence of the oxo ligand causes the Re−Py bond to elongate and then break. Finally, internal electron transfer and ring-closure take place, giving rise to the Re(VII) catecholate product. In the reverse direction, the identity of the ancillary dithiolato ligand has but a minimal effect on the rate constant, with an even smaller effect from the identity of the entering pyridine ligand. The reverse reaction requires dechelation of the catecholate in order for Py to add. The more electron density on rhenium (edt > mtp), the faster is dechelation. This step must be very slow when the leaving group is DBQ because the rate of the reverse reaction is too low to be measured. We propose that the first reaction step is an equilibrium that is established much more rapidly than the rate-controlling step. The combination of the turnstile rotation, Re−Py bond-breaking and -making, and the internal electronic transformations are thus rate-controlling in both directions.

Comments on Structure. The reaction product is to our knowledge the first example of a rhenium(VII) dithiolate complex that does not immediately release the organic disulfide by internal electron transfer. For example, the Re(VII) compound $\mathrm{MeRe(O)_2(mtp)OPy}$, unless intercepted by a second phosphine reagent, undergoes irreversible decomposition:[5,36] Our assignment of MeReO(dithiolate)Cat complexes as being catecholates in fact follows from results presented by other investigators. The Re(VII) catecholate complexes that have been previously reported are all intensely colored blue and purple compounds.[24,25] The crystal structures define the C−O bond lengths indicative of a catechol (133.7−138.7 pm) as opposed to a semiquinone (127.2−131.2 pm).[37] As of yet, all complexes of rhenium in high oxidation states with quinone-based ligands exist as catecholate complexes in the solid state.[16−18,20−22,24,37]



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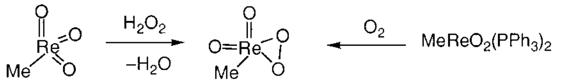
Catecholates can donate more π-electron density than semiquinones and are therefore favored by metals in a high oxidation state. Pierpont suggests that the charge distribution in such compounds is related to the energies of the quinone π-orbitals and the metal d-orbitals.[37] The charge will reside in the orbitals of lower energy, in this case the metal quinone orbitals, giving rise to metal catecholate compounds.

Other Considerations. This is the first case in which "stable" Re(VII) dithiolate compounds have been obtained. Even so, the complexes do not persist indefinitely. The dithiolate ligand does slowly become oxidized to the disulfide, $MeReO_3$ being formed concurrently. The formation of metal−oxo bonds is an additional driving force. Our data suggest that quinones may be able to trap Re(V) intermediates.

The condensation of catechols with Re(VII) and the oxidation of Re(V) by quinones bear a conceptual relation to the respective reactions with H_2O_2 and O_2. The condensation reaction between $MeReO_3$ and hydrogen peroxide forms a cyclic peroxide.[38−41] Also, $MeReO_2$ reacts with O_2 to give the same product, albeit with complications from the phosphine.[42]



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Supporting Information Available: Figures and tables showing the electronic spectra, the analysis of kinetic data, and time−course data for reactions of MeReO(dithiolate)Py with phenanthrenequinone. This material is available free of charge via the Internet at http://pubs.acs.org.

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