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Photoinduced Proton Transfer between Transdioxorhenium(V) and Metal Hydrides: A New Method for Quantitating Kinetic Acidities

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Abstract: The $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz,yz})^1$ excited state of *trans*-$ReO_2(py)_4^+$ is quenched by proton transfer from Tp′Mo$(CO)_3H$ (Tp′ = hydridotris[(3,5-dimethyl)pyrazolyl]borate) and $CpM(CO)_3H$ (M = Cr, Mo, W). The pK_a's and proton self-exchange rate constants (k_{22}) of these metal hydrides are well characterized in acetonitrile. The rate constants (k_Q) for quenching of $ReO_2(py)_4^{+*}$ by these complexes were determined by Stern–Volmer quenching. The relative rate constants for the four metal hydrides are described by the Marcus cross relation, which predicts that a plot of $\log(k_Q/k_{22}^{1/2})$ versus pK_a will be linear with a slope of 1/2. In fact, a linear correlation is observed with a slope of 0.53. From this relationship, values for k_{22} can be calculated for metal hydrides where k_Q and pK_a are known. This method has been applied to $TpMo(CO)_3H$ and $Mn(CO)_5H$ (Tp = hydridotris(pyrazolyl)borate), which give k_{22}'s of 200 and 1200 $M^{-1}\ s^{-1}$, respectively. These rate constants are consistent with the steric and electronic factors that can be expected to govern the kinetic acidities. The isotope effects for quenching by the $CpM(CO)_3H$ complexes are the same within experimental error for all three complexes, as predicted by the Marcus cross relation and the known isotope effects on M–H self exchange. These data give an isotope effect for $ReO(OH)(py)_4^{+*}$ of 1.2 ± 0.1, which is consistent with the fast ($10^7\ M^{-1}\ s^{-1}$) self-exchange estimated by other methods.

Hydrogen abstraction by metal-oxo complexes plays an important role in biochemistry and catalysis.[1–4] Upon transfer of hydrogen (or alkyl)[3] to a doubly or triply bonded oxo ligand, the extent of multiple bonding is reduced.[5] This change in multiple bonding will alter the energy of the metal orbitals participating in the hydrogen transfer. We have initiated a program to study these effects on the simplest level using excited-state proton transfer reactions of transdioxorhenium(V).[6–8] The lowest-lying excited state of complexes based on *trans*-$ReO_2(py)_4^+$ is generated via promotion of a nonbonding electron from the d_{xy} orbital to the $d_{xz,yz}$ level, which is formally Re–O antibonding.[9] There is considerable interaction of the d_{xy} orbital with the π^* orbitals of the pyridine ligands, which allows the photophysics to be tuned finely by substitution on the pyridine ligands.[10–12] This delocalization also imparts a great deal of charge-transfer character to the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz,yz})^1$ transition ($\epsilon = 1200\ M^{-1}\ cm^{-1}$). There is a significantly greater electron density on oxygen in the excited state compared to the ground state, which renders the oxo ligands susceptible to protonation.[6]

The excited state of $ReO_2(py)_4^+$ is quenched by a wide variety of proton donors, including simple nitrogen and oxygen acids,[6,7] carbon acids, and metal hydrides.[8] We have shown that Marcus theory describes the free energy dependence of proton transfer in each of these systems. For "fast" nitrogen and oxygen acids, the total intrinsic barrier is small, so ΔG is comparable to the reorganizational energy. In this case, the kinetics can be analyzed by eq 1.[7]

$$\Delta G^{\ddagger} = \lambda/4(1 + \Delta G/\lambda)^2 \qquad (1)$$

Metal hydride acids exhibit large barriers to proton transfer due to the electronic reorganization required to convert a partially negative hydride ligand to a proton.[13–15] As a result, $\Delta G \ll \lambda$, so the kinetics can be analyzed according to[8]

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2} \qquad (2)$$

where k_{11} and k_{22} are the proton self-exchange rate constants for $ReO(OH)(py)_4^{+*}$ and the metal hydrides, respectively, and K_{12} is the equilibrium constant for the proton-transfer reaction (eqs 3–5).

$$ReO(OH)(py)_4^{2+*} + ReO_2(py)_4^{+*} \xrightleftharpoons{k_{11}} ReO_2(py)_4^{+*} + ReO(OH)(py)_4^{2+*} \qquad (3)$$

$$M{-}H + M^- \xrightleftharpoons{k_{22}} M^- + M{-}H \qquad (4)$$

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$$\text{ReO}_2(\text{py})_4^{+*} + \text{M-H} \overset{K_{12}}{\rightleftharpoons} \text{ReO(OH)(py)}_4^{2+*} + \text{M}^- \quad (5)$$

We have reported previously that the complexes $\text{CpM(CO)}_3\text{H}$ (M = Cr, Mo, W), for which k_{22} and pK_a are known in acetonitrile,[13,14] quench $\text{ReO}_2(\text{py})_4^{+*}$ and that the relative rates are described by eq 2. The absolute rate constants for proton transfer between these complexes are also described by eq 2.[16] We report here on studies of additional metal hydride quenchers and use the quenching rate constants to establish a kinetic acidity series by which k_{22} can be determined quantitatively for metal hydrides of known pK_a. This simple procedure should permit assessment of the kinetic acidities of a wide variety of metal hydrides. We also show here how this series can be used, in conjunction with rate data on oxygen and nitrogen acids,[7] to understand the absolute rate constants and the rate of self-exchange in $\text{ReO}_2(\text{py})_4^{+*}$ (k_{11}). Finally, the isotope effects for quenching by $\text{CpM(CO)}_3\text{D}$ are consistent with these analyses.[17]

Experimental Section

All operations were performed using vacuum line or dry box techniques. Acetonitrile for photochemical measurements was purified by refluxing over P_2O_5 and CaH_2 and degassing by five freeze−pump−thaw cycles. All starting materials were purchased from Aldrich and used as received unless specifically indicated.

The complexes $\text{CpM(CO)}_3\text{H}$,[18,19] $\text{Mn(CO)}_5\text{H}$,[20] $\text{TpMo(CO)}_3\text{H}$,[21] and $\text{Tp'Mo(CO)}_3\text{H}$[22] (Tp = hydridotris(pyrazolyl)borate, Tp′ = hydridotris[(3,5-dimethyl)pyrazolyl]borate) were prepared and purified according to published procedures and characterized by proton NMR. The metal deuterides $\text{CpM(CO)}_3\text{D}$ were prepared according to published procedures.[19,23] The extent of deuteration was assessed by proton NMR and integration of the metal-hydride resonance compared to the Cp protons, which showed that all three complexes were at least 92% deuterated.

Quenching rate constants were measured according to the Stern−Volmer relation

$$I^\circ/I = 1\ k_Q\tau[\text{M-H}] \quad (6)$$

where I° is the emission intensity for $\text{ReO}_2(\text{py})_4^{+*}$ in the absence of quencher, I is the emission intensity in the presence of a concentration [M−H] of metal hydride, and τ is the emission lifetime of $\text{ReO}_2(\text{py})_4^{+*}$ (10 μs).[24] The protonated excited state, $\text{ReO(OH)(py)}_4^{2+*}$, is extremely short-lived, so the Stern−Volmer rate constant (k_Q) gives the actual rate of protonation, as discussed elsewhere.[5,7] Emission spectra were collected in inert-atmosphere cells on a SPEX Fluoromax single-photon counting emission spectrometer, and at least five points were collected at concentrations where I°/I reached a maximum value of at least 2. For the metal deuterides, quenching rate constants $k_Q{}^D$ were corrected for residual metal hydride according to

$$I^\circ/I = 1\ k_Q{}^H\tau[\text{M-H}] + k_Q{}^D\tau[\text{M-D}] \quad (7)$$

where $k_Q{}^H$ was the Stern−Volmer rate constant for the authentic metal hydride; and the relative concentrations of [M−H] and [M−D] were determined from the NMR spectrum of the metal deuteride, as described above. Even though this correction was applied, rate constants for deuterides were obtained only on samples that were >92% deuterated. Determination of quenching rate constants using lifetime data (i.e., τ°/τ) does not change the observed rate constants, as discussed elsewhere.[7,8]

Table 1. Proton-Transfer Rate Constants for Quenching of $\text{ReO}_2(\text{py})^{+*}$

quencher	pK_a(M−H)	k_{22} ($M^{-1}\ s^{-1}$)	k_Q ($M^{-1}\ s^{-1}$)
$\text{Tp'Mo(CO)}_3\text{H}$	10.2[a]	3.5[a]	4.8×10^8
$\text{TpMo(CO)}_3\text{H}$	11.3[a]	(200)[b]	7.9×10^8
$\text{CpCr(CO)}_3\text{H}$	13.3[c]	18 000[c]	5.5×10^8[d]
$\text{CpMo(CO)}_3\text{H}$	13.9[c]	2500[c]	8.9×10^7[d]
$\text{Mn(CO)}_5\text{H}$	14.2[e]	(1200)[b]	5.6×10^7
$\text{CpW(CO)}_3\text{H}$	16.1[c]	650[c]	5.2×10^6[d]

[a] Taken from ref 22. [b] Calculated from eq 2 and Figure 1. [c] Taken from ref 25. [d] Taken from ref 8. [e] Taken from ref 14.

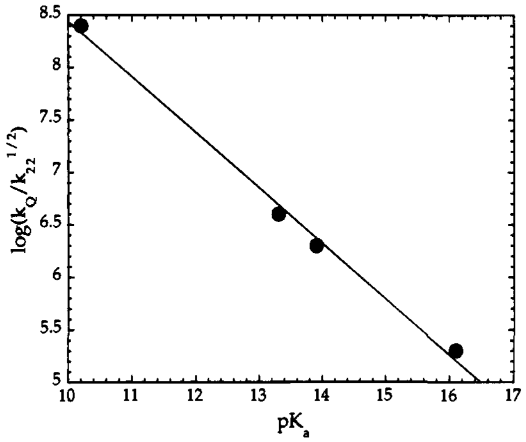

Figure 1. Plot of $\log(k_Q/k_{22}{}^{1/2})$ versus the pK_a of the metal-hydride quencher. The solid line is a linear least-squares fit with a slope of −0.53 and y-intercept of 13.6. This line was used to calculate the k_{22}'s given in Table 1 for $\text{Mn(CO)}_5\text{H}$ and $\text{TpMo(CO)}_3\text{H}$.

Results and Discussion

Quenching by Metal Hydrides. The proton-transfer rate constants for quenching of $\text{ReO}_2(\text{py})_4^{+*}$ by $\text{CpM(CO)}_3\text{H}$ were determined previously and are given for reference in Table 1.[8] The k_{22}'s for these three complexes are correlated with the corresponding pK_a's such that the strongest acid exhibits the fastest k_{22}. Recently, the self-exchange rate constant for $\text{Tp'Mo(CO)}_3\text{H}$ was determined.[22] Even though this complex is a stronger acid than any of the Cp complexes, it exhibits the slowest k_{22} due to the steric constraints of the Tp′ ligand. This difference provides an important test for our analysis, because the slow k_{22} suggests that proton transfer onto $\text{ReO}_2(\text{py})_4^{+*}$ should also be attenuated, according to eq 2. The rate constant for quenching of $\text{ReO}_2(\text{py})_4^{+*}$ by $\text{Tp'Mo(CO)}_3\text{H}$ was 4.8×10^8 $M^{-1}\ s^{-1}$, which is actually slightly slower than that for $\text{CpCr(CO)}_3\text{H}$, which is a weaker acid by nearly 4 pK_a units.

According to eq 2, a plot of $\log(k_Q/k_{22}{}^{1/2})$ versus pK_a should be linear with a slope of −1/2. Shown in Figure 1 is such a plot for $\text{CpM(CO)}_3\text{H}$ and $\text{Tp'Mo(CO)}_3\text{H}$, which is in fact linear with a slope of −0.53. The k_{22}'s determined for the four complexes shown in Figure 2 were determined by temperature-dependent proton NMR of solutions of the metal hydride complex and the deprotonated anion.[17,22,25] These experiments require that the complex contains other protons, such as those of the Cp or Tp′ ligands. A simpler method for determining k_{22}'s for metal hydrides of known pK_a is presented by Figure 1, which shows that the rate constant for quenching of $\text{ReO}_2(\text{py})_4^{+*}$ and pK_a are related by k_{22}. Thus, if the pK_a is known,

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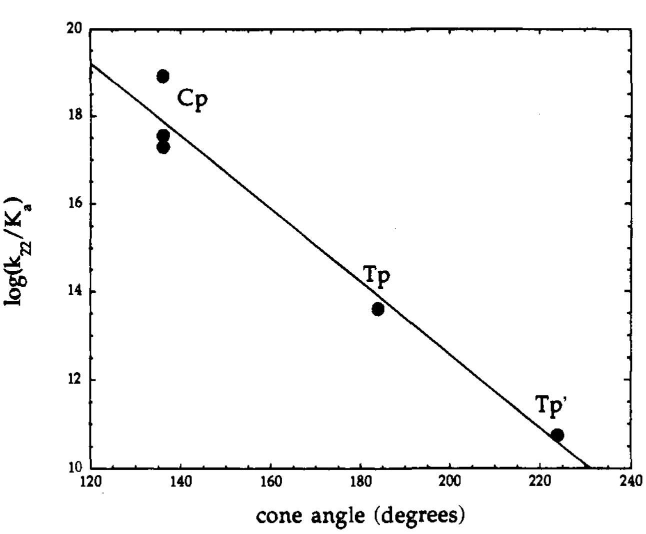

Figure 2. Plot of $\log(k_{22}/K_a)$ versus cone angle for the metal hydride quenchers $LM(CO)_3H$ where L = Cp, Tp, or Tp′. An equally good correlation was obtained if $\log(k_Q/K_a)$ was plotted, which follows from the linear correlation seen in Figure 1.

k_{22} can be determined using a simple Stern–Volmer quenching experiment and Figure 1.

The complex $Mn(CO)_5H$ exhibits a pK_a of 14.2[14] and quenches $ReO_2(py)_4{}^{+*}$ with a rate constant of 5.6×10^7 M^{-1} s^{-1}. Because the complex does not contain any other protons, k_{22} cannot be determined by NMR; however, a k_{22} of 1200 M^{-1} s^{-1} can be estimated from Figure 1. This value of k_{22} is slightly less than that for $CpMo(CO)_3H$, which is a slightly stronger acid. It therefore appears that the kinetic and thermodynamic acidity of $Mn(CO)_5H$ are correlated in the same way as for $CpM(CO)_3H$[14] with no interference from steric effects. Norton and co-workers have shown that $Mn(CO)_5H$ fits on a linear kinetic acidity series determined for protonation of aniline by a series of metal hydrides, none of which would expected to exhibit attenuation of k_{22} by steric effects.[17]

The method of determining k_{22} by quenching of $ReO_2(py)_4{}^{+*}$ was also applied to the complex $TpMo(CO)_3H$. This complex exhibits a pK_a of 11.3[22] and quenches $ReO_2(py)_4{}^{+*}$ with a rate constant of 7.9×10^8 M^{-1} s^{-1}. This rate constant is somewhat higher than that for $Tp'Mo(CO)_3H$, even though the Tp′ complex is a stronger acid by one unit, suggesting that the steric constraints for $TpMo(CO)_3H$ are not as severe as for $Tp'Mo(CO)_3H$. The rate constants are therefore consistent with the cone angles for Tp (184°) and Tp′ (224°)[26] in indicating greater steric constraints for Tp′. Accordingly, a k_{22} for $TpMo(CO)_3H$ of 200 M^{-1} s^{-1} is calculated from Figure 1. As for the Tp′ complex, this value is significantly lower than those for the $CpM(CO)_3H$, even though the Cp complexes are weaker acids. Thus, there is still significant steric attenuation of k_{22} for $TpMo(CO)_3H$, although not as severe as for $Tp'Mo(CO)_3H$.

Cone angles are frequently used to assess steric attenuation of rates and equilibria.[27] The cone angles for Cp, Tp, and Tp′ are 136°, 184°, and 224°, respectively.[26] Since the k_{22}'s for the Cp complexes are correlated with the thermodynamic acidity, it is reasonable to compare the quantity $\log(k_{22}/K_a)$ with the cone angle of the capping ligand to assess the steric effects. Shown in Figure 2 is a plot of this quantity versus the cone angle of Cp, Tp, or Tp′. The linear correlation supports the idea that determining k_{22}'s from quenching of $ReO_2(py)_4{}^{+*}$ properly accounts for steric effects. An equally good linear correlation was observed between $\log(k_Q/K_a)$ and cone angle, which follows from the linear correlation seen in Figure 1.

Table 2. Isotope Effects on Proton-Transfer Quenching of $ReO_2(py)_4{}^{+*}$

quencher	k^D (M^{-1} $s-^1$)	k^H/k^D	$k_{22}{}^H/k_{22}{}^{D\,a}$	$k_{11}{}^H/k_{22}{}^D$
$CpCr(CO)_3H$	2.6×10^8	2.1	3.6	1.2
$CpMo(CO)_3H$	4.0×10^7	2.2	3.7	1.2
$CpW(CO)_3H$	2.5×10^6	2.1	3.7	1.1

[a] Taken from reference 17.

Isotope Effects. The rate constants for quenching of $ReO_2(py)_4{}^{+*}$ by the complexes $CpM(CO)_3D$ are given in Table 2 along with the calculated isotope effects k^H/k^D. The isotope effect is the same for all three reactions and relatively small (2.1–2.2). If the driving force is the same for both proton and deuteron transfer (i.e., $K_{12}{}^D = K_{12}{}^H$), the isotope effect should be described by

$$k^H/k^D = [(k_{11}{}^H/k_{11}{}^D)(k_{22}{}^H/k_{22}{}^D)]^{1/2} \tag{8}$$

where the H and D superscripts indicate parameters associated with proton or deuteron transfer, respectively. Since the kinetic isotope effects for the self-exchange reactions of the metal hydrides ($k_{22}{}^H/k_{22}{}^D$) are known,[17] the isotope effect on self-exchange for $ReO_2(py)_4{}^{+*}$ ($k_{11}{}^H/k_{11}{}^D$) can be calculated from eq 8.

The known isotope effects for the metal hydrides are given in Table 2 and are invariant within experimental error as a function of driving force. The measured isotope effects should therefore be the same for all three complexes, as is observed. The isotope effect on $ReO_2(py)_4{}^{+*}$ self-exchange is calculated from eq 8 to be $k_{22}{}^H/k_{22}{}^D = 1.2 \pm 0.1$. This small isotope effect implies that k_{22} is a fast proton transfer.[28]

Relationship between Metal Hydride and Fast Acids. The proton-transfer quenching of $ReO_2(py)_4{}^{+*}$ by nitrogen and oxygen acids has been analyzed in terms of eq 1.[7] In practice, this analysis involves fitting the diffusion-corrected rate constants k_Q' to the relation:

$$RT \ln k_Q' = RT \ln k_Q'(0) - \Delta G/2 - \Delta G^2/4\lambda \tag{9}$$

where $k_Q'(0)$ is the hypothetical diffusion-corrected rate constant at $\Delta G = 0$. It therefore follows from eq 2 that $k_Q'(0) = (k_{11}k_{22})^{1/2}$. Fitting of the rate constants for cationic nitrogen acids to eq 9 gives pK_a(Re) = 19.1 and $k_Q'(0) = 8.1 \times 10^7$ M^{-1} s^{-1}.[7] The parameter λ is held fixed during the fitting at a value of 4 kcal/mol, which was determined separately by temperature-dependent quenching. We have pointed out previously that if k_{11} for the nitrogen acids is assumed to be 10^9 M^{-1} s^{-1},[28] k_{11} for $ReO(OH)(py)_4{}^{+*}$ can be estimated from $k_Q'(0)$ to be about 10^7 M^{-1} s^{-1}. Using the determined pK_a(Re) = 19.1 from eq 9, we can now calculate the explicit K_{12} for each reaction to obtain a more precise k_{11} of $(3 \pm 1) \times 10^7$ M^{-1} s^{-1} from eq 2. Roodt and co-workers have recently estimated the upper limit of the self-exchange rate constant for the ground state of the isoelectronic complex $ReO(OH)(CN)_4{}^{2-}$ as 5×10^7 M^{-1} s^{-1}.[29]

A number of self-consistent parameters are now available on the dynamics of the $ReO(OH)(py)_4{}^{+*}$ self-exchange. The low reorganizational energy (λ = 4 kcal/mol) for fast acids implies that k_{22} should be relatively fast. The self-exchange rate constant calculated from the pK_a(Re) and the metal hydride data is 3×10^7 M^{-1} s^{-1}, and a similar k_{22} is estimated from the

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$k_Q'(0)$ for fast acids. Finally, the small isotope effect reported here also points to a relatively rapid proton transfer for $ReO(OH)(py)_4^{+*}$ self-exchange. These observations then suggest that the electronic reorganization associated with breaking the Re=O multiple bond does not dictate a particularly large barrier to proton transfer. However, the electronic reorganization is evident in the absorption energies for the ligand-field transitions for $ReO_2(py)_4^+$ and $ReO(OH)(py)_4^+$, which are 22 700 and 18 300 cm^{-1}, respectively.[30] Protonation deactivates the excited state and precludes emission, but this effect may also arise from changes in the vibrational degrees of freedom in addition to changes in the electronic structure. Nevertheless, the photophysical properties of the complex are apparently much more sensitive to the electronic reorganization than the proton-transfer kinetics.

Norton and co-workers have reported that protonation of bridging oxo ligands in the ground state is considerably slower than the k_{22} determined here for $ReO(OH)(py)_4^{+*}$.[13,31] This difference may occur partly because in the excited state of $ReO_2(py)_4^+$ much of the electronic reorganization needed for protonation has already occurred upon excitation. The ligand-field excitation involves a decrease in the Re=O bond order, because the $d_{xz,yz}$ level is formally Re–O antibonding. Accordingly, Franck–Condon analysis shows that excitation leads to a lengthening of the Re–O bond.[9] These factors may cause the excited state to resemble the protonated form more closely compared to the ground state. Therefore, much of the electronic reorganization required to protonate the metal–ligand bond is accomplished by excitation before the rate constants are actually measured. We have shown that complexes that exhibit greater distortion in the Re=O coordinate upon excitation are quenched more efficiently after correction for changes in driving force,[7] which is consistent with the idea that the electronic structure of the excited state plays an important role in establishing the rapid k_{22}.

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