J. Am. Chem. Soc. **1993**, *115*, 11048–11049

Excited-State Quenching through Large Intrinsic Barriers: Proton-Transfer Reactions of Metal Hydrides

James G. Goll, Wentian Liu, and H. Holden Thorp*

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27599-3290

Received June 1, 1993

The application of Marcus theory to understanding bimolecular excited-state quenching has been pursued vigorously, especially for electron-transfer reactions.[1-4] Most studies involve the analysis of the driving-force dependence of the quenching rate constant among a series of homologous quenchers using the expression

$$RT \ln k_Q' = RT \ln k_Q'(0) - \Delta G/2 - \Delta G^2/4\lambda \qquad (1)$$

where k_Q' is the quenching rate constant corrected for diffusion, λ is the reorganizational energy, and ΔG is the free energy of the excited-state reaction.[1] The quantity $k_Q'(0)$ is defined as

$$k_Q'(0) = (k_{11}k_{22})^{1/2} \qquad (2)$$

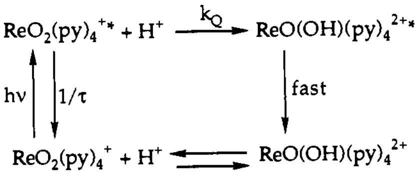
where k_{11} and k_{22} are the self-exchange rate constants for the quencher and the excited state, respectively. In general, members of a homologous series of quenchers will have similar k_{11}'s that are usually fast ($\sim 10^9$ M^{-1} s^{-1}),[1,2] suggesting a small intrinsic barrier to quenching. The applicability of eq 1 to excited-state quenching in a homologous series suggests that eq 3 should describe any general excited-state quenching reaction,

$$k_Q = (k_{11}k_{22}K_{eq})^{1/2} \qquad (3)$$

where K_{eq} is the equilibrium constant for the excited-state reaction.[4] To our knowledge the applicability of eq 3 in cases where k_{11} is slow and significantly different between quenchers has not been demonstrated for excited-state reactions.

Application of Marcus theory to excited-state proton transfer reactions is difficult in organic systems, such as styrenes, because excited-state distortions lead to values for α ($= d\Delta G^{\ddagger}/d\Delta G$) that are significantly less than 0.5 at $\Delta G = 0$, which must be the case for eq 1 to apply.[5,6] We have been studying excited-state proton-transfer reactions of the *trans*-dioxorhenium(V) complex $ReO_2(py)_4^+$ in acetonitrile solution.[7] We expected this complex to exhibit smaller excited-state distortions than related organic species and, hence, more symmetrical proton transfers. The long-lived $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz,yz})^1$ excited state is efficiently quenched by proton transfer from water and other proton donors with a large deuterium isotope effect.[7,8] The collective evidence points to the quenching mechanism shown in Scheme 1, where the transfer of a proton to $ReO_2(py)_4^{+*}$ (k_Q) leads to the formation of a very short-lived excited state, $ReO(OH)(py)_4^{2+*}$.[9] The protonated excited state decays to the ground state before an excited-state acid–base equilibrium can be established, and proton transfer therefore leads directly to excited-state deactivation.

Scheme I



Two factors complicate study of excited-state proton-transfer quenching relative to study of related electron-transfer reactions: the existence of hydrogen-bonded intermediates and a greater variability of self-exchange rate constants for potential acid quenchers.[6,11,12] For example, the driving force dependence reported previously of the quenching of $ReO_2(py)_4^{+*}$ by common oxygen and nitrogen acids is suggestive of the behavior predicted by eq 1, but analysis using eq 1 has been hampered by concerns over hydrogen bonding of the acid to the ground state of $ReO_2(py)_4^+$ prior to excitation.[7] In fact, quenching by 2,6-di-*tert*-butylpyridinium, which is sterically prohibited from forming a hydrogen bond, is an order of magnitude slower ($k_Q = 1.8 \times 10^8$ M^{-1} s^{-1}) than quenching by hydrogen-bonding acids with similar pK_a's,[7] indicating that hydrogen-bonded species can indeed mediate the proton transfer. Carbon acids are less likely to form hydrogen bonds; however, proton-transfer reactions of carbon acids proceed through large intrinsic barriers,[6,13] and these quenchers consequently exhibit slow self-exchange rate constants. As a result, k_Q for nitroethane is 4.9×10^4 M^{-1} s^{-1},[14] which is 4 orders of magnitude slower than than those for nitrogen or oxygen acids of similar pK_a that exhibit fast self-exchange.[7]

The observation of slow quenching with nitroethane suggests that eq 3 may describe k_Q for excited-state proton transfer by quenchers of known k_{11}. In order to confirm this dependence, a family of quenchers must be chosen with pK_a's and k_{11}'s that are known in acetonitrile. To simplify the analysis, these quenchers should not form hydrogen bonds to the oxo groups of $ReO_2(py)_4^+$. The kinetic and thermodynamic acidities of the metal hydrides $CpM(CO)_3H$ (M = Cr, Mo, W; Cp = C_5H_5) have been thoroughly characterized in acetonitrile,[10,11] and proton-transfer reactions of these complexes do not proceed through hydrogen-bonded intermediates.[15] Recent studies have shown that the kinetics of proton transfer between hydrides and anions of these complexes are described by eq 3.[9] Because of extensive electronic reorganization of the M–H functionality upon deprotonation, intrinsic

---

(1) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(2) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027. Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7349.

(3) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(4) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(5) Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6511. McEwen, J.; Yates, K. *J. Am. Chem. Soc.* **1987**, *109*, 5800. Yates, K. *J. Phys. Org. Chem.* **1989**, *2*, 300.

(6) Application of Marcus theory to ground-state (and some excited-state) proton transfers, of course, has been successful, see: Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285. Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475. Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

(7) Liu, W.; Welch, T. W.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 4044.

(8) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364. Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.

(9) The short excited-state lifetime of $ReO(OH)(py)_4^{+*}$ is supported by the lack of any observed emission from solutions of authentic ReO(OH)$(py)_4^{2+}$ [10a] and by nanosecond transient absorbance experiments, which show no evidence for the protonated excited state. Also, the excited-state energy for $ReO(OH)(py)_4^{2+}$ is much lower (2700 cm^{-1})[10a] than that for $ReO_2(py)_4^+$, which suggests a shorter lifetime according to the energy-gap law.[10b] Finally, Hupp and co-workers have prepared $ReO(OMe)^{2+}$ complexes that have absorption energies identical to the analogous ReO_2^+ complexes, and these complexes have no measurable excited-state lifetime.[10c] The ground-state pK_a of $ReO(OH)(py)_4^{2+}$ is −0.3 in 1:1 CH_3CN/H_2O.[10d]

(10) (a) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (c) Ram, M. S.; Skeens-Jones, L. M.; Johnson, C. S.; Zhang, X. L.; Hupp, J. T. Unpublished results. (d) Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y.-H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928.

(11) Kristjánsdóttir, S. S.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4366.

(12) Eddin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

(13) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224.

(14) In water, nitroethane has a pK_a of 8.57 (Harris, D. C. *Quantitative Chemical Analysis*; W. H. Freeman and Company: San Francisco, 1982) and a λ of 17 kcal/mol;[13] however, these quantities are unknown in acetonitrile.

(15) Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357. The formation of weak hydrogen bonds between Cp_2OsH^+ and phosphine oxides has recently been reported (Epstein, L. M.; Shubina, E. S.; Krylov, A. N.; Keindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1993**, *447*, 277); however, a cationic complex would be a much better hydrogen-bond donor than a neutral complex, such as $CpM(CO)_3H$.

0002-7863/93/1515-11048$04.00/0

barriers to proton transfer are large (9-14 kcal/mol) and k_{11}'s are consequently slow.

All three metal–hydride complexes quench the emission of $ReO_2(py)_4^{+*}$ following Stern–Volmer kinetics ($k_Q(Cr) = 5.5 \times 10^8$ M^{-1} s^{-1}, $k_Q(Mo) = 8.9 \times 10^7$ M^{-1} s^{-1}, $k_Q(W) = 5.2 \times 10^6$ M^{-1} s^{-1}).[16] We do not know the precise pK_a of $ReO(OH)(py)_4^{+*}$ or the self-exchange rate constant for excited-state proton transfer, so we cannot apply eq 3 directly, where $K_{eq} = K_a(CpM(CO)_3H)/K_a(ReO(OH)(py)_4^{2+*})$. However, $K_a(ReO(OH)(py)_4^{2+*})$ and $k_{22}(ReO_2(py)_4^{+*})$ can be canceled by determining the ratio of any two quenching rate constants. This ratio can thereby be calculated from only the parameters of the metal–hydride quenchers (M1 and M2) according to

$$k_Q(M1)/k_Q(M2) = [(k_{11}(M1)\,K_a(M1))/(k_{11}(M2)\,K_a(M2))]^{1/2} \quad (4)$$

Excellent agreement between the measured and calculated ratios is observed, as shown in Table I.

The agreement shown in Table I makes a number of interesting points. First, this is a unique quantitative demonstration that excited-state proton transfer is described by Marcus theory, which apparently obtains because (i) there is no hydrogen bonding, (ii) there is relatively little excited-state distortion in $ReO_2(py)_4^{+*}$ compared to related organic excited states, and (iii) the kinetic and thermodynamic acidities of the quenchers are fully characterized in acetonitrile. Second, k_{11}'s have been determined only for the three metal–hydrides described here, because the cyclopentadienyl protons permit kinetic studies using NMR line-broadening.[12] There is no convenient method for determining k_{11}'s for many other metal–hydrides, such as $H_2Fe(CO)_4$ and $HMn(CO)_5$. By comparing the quenching rate constant for any metal–hydride of known pK_a to the data shown in Table I, the k_{11} of the metal–hydride might be estimated. Thus, in addition to elucidating the fundamentals of excited-state proton transfer, studies of $ReO_2(py)_4^{+*}$ may also provide a convenient means for quantitating the kinetic acidity of metal–hydrides and other novel acids.

Table I. Ratios of Stern–Volmer Rate Constants for Quenching of $ReO_2(py)_4^{+*}$

	calcd using eq 4[a]	measd
$k_Q(Mo)/k_Q(W)$	24	17
$k_Q(Cr)/k_Q(W)$	130	110
$k_Q(Cr)/k_Q(Mo)$	5.4	6.2

[a] Calculated using $k_{11}(Cr) = 18\,000$ M^{-1} s^{-1}, $k_{11}(Mo) = 2500$ M^{-1} s^{-1}, $k_{11}(W) = 650$ M^{-1} s^{-1}; p$K_a(Cr) = 13.3$, p$K_a(Mo) = 13.9$, p$K_a(W) = 16.1$.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. H.H.T. is a NSF Presidential Young Investigator and a Fellow of the David and Lucile Packard Foundation. Helpful discussions with Professors Jack Norton and Joe Hupp are also acknowledged.

---

(16) Metal–hydride complexes were prepared according to published procedures[17] and stored in a drybox. The $[ReO_2(py)_4](PF_6)$ complex was prepared according to published procedures.[8] Quenching experiments were performed by addition of known amounts of quencher to acetonitrile solutions of $[ReO_2(py)_4](PF_6)$. All handling of reagents was performed on a high-vacuum line or in a drybox. Acetonitrile was distilled from P_2O_5 and stored under vacuum over CaH_2. Emission spectra were measured on a SPEX Fluoromax, and quenching rate constants were determined at room temperature according to the Stern–Volmer equation: $I^\circ/I = 1 + k_Q\tau[Q]$, where $\tau = 10$ μs[8] and [Q] is the concentration of metal–hydride. Previous experiments have shown that both emission intensity and lifetime quenching give the same rate constants for proton transfer reactions.[7]

(17) Keppie, S. A.; Lappert, M. F. *J. Organomet. Chem.* **1969**, *19*, 5.