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Excited-State Proton Transfer in *trans*-Dioxorhenium(V)

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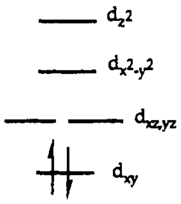
Among axially compressed d^1 and d^2 ions,[1] the electronic properties of *trans*-dioxorhenium(VI/V) cores are particularly amenable to study by numerous spectroscopic methods.[2–5] The emissive excited state of the d^2 ion *trans*-$ReO_2(py)_4^+$ (**1**) is an excited-state reductant and a sensitive probe of hydrophobic binding regions.[3,6] This ^3E_g excited state is created by promotion of an electron from the nonbonding d_{xy} level to the formally Re–O π-antibonding $d_{xz,yz}$ level:



Franck–Condon analysis of the vibronic structure seen in low temperature absorption spectra of **1** demonstrates that the Re–O bond lengthens by 0.07 Å upon population of the ^3E_g state, consistent with the electronic assignment.[2] The excited state is efficiently quenched by water ($k_Q = 9.5 \times 10^5$ M^{-1} s^{-1}), which is responsible for its utility as a probe of hydrophobic binding regions in surfactant solutions,[6] layered oxides,[7] polymer membranes,[8] and DNA.[9] To date, the mechanism of this quenching reaction has remained unclear.

Proton transfer was initially ruled out as the quenching mechanism because the pyridinium ion apparently failed to quench the excited state efficiently, even though its pK_a is nearly 9 units lower than that of water.[2] Proton NMR experiments suggest, however, that alcohols hydrogen bond to the ground state of **1** via the hydroxyl proton.[3] It seems likely that promotion of an electron from a metal-based orbital to an orbital with appreciable oxygen character would render the oxo ligands more basic and thereby susceptible to protonation, particularly by an acid to which a hydrogen bond exists. We report here that pyridinium ion and other organic acids are effective quenchers of the excited state of **1** in acetonitrile by a proton-transfer mechanism.

Quenching of the emission intensity of **1*** in acetonitrile solution was observed for all of the acids given in Table I.[10,11] The reported rate constants were obtained using the Stern–Volmer relation,[14] which was strictly obeyed in all of our measurements. There is a clear trend toward the diffusion-controlled limit as the pK_a of the acid decreases, consistent with a greater driving force for proton transfer as the pK_a is lowered.[15] A plot of log k_Q versus the aqueous pK_a of the acid quenchers is shown in Figure 1. As the driving force for proton transfer increases, the data follow what appears to be a parabolic dependence that levels off at k_Q $\sim 10^9$ M^{-1} s^{-1}. This plot bears a striking resemblance to related plots for bimolecular excited-state electron-transfer reactions, where rate constants similarly increase with increasing driving force and level off near the diffusion-controlled limit.[15,16]

Table I. Rate Constants for Quenching of $ReO_2(py)_4^{+*}$ by Organic Acids

quencher	pK_a[a]	k_Q (M^{-1} s^{-1})
water	15.7	9.5×10^5
1,4-dihydro-4-imino-1-methylpyrimidine hydroiodide	12.2[b]	3.5×10^7
triethylammonium hexafluorophosphate	10.7	1.6×10^8
trimethylammonium tetraphenylborate	9.8	3.4×10^8
ammonium hexafluorophosphate	9.2	3.9×10^8
3-nitrophenol	8.4	5.3×10^8
4-nitrophenol	7.2	1.2×10^9
pyridinium *p*-toluenesulfonate	5.2	9.5×10^8
benzoic acid	4.2	1.3×10^9
4-nitrobenzoic acid	3.4	8.8×10^8

[a] Reference 12 unless noted. [b] Reference 13.

Further evidence for excited-state proton transfer can be obtained by varying the pK_a of the metal complex rather than the quencher. The ground-state pK_a of $ReO(OH)(py)_4^{2+}$ is –0.3, while the ground-state pK_a of $ReO(OH)(4\text{-}OMe\text{-}py)_4^{2+}$ is 0.5 and that of $ReO(OH)(3\text{-}Cl\text{-}py)_4^{2+}$ is –0.5.[17] The 4-OMe-py[18] and 3-Cl-py[19] complexes were prepared by literature methods and exhibit emission maxima in CH_3CN solution of 717 nm for the 4-OMe-py complex[20] and 646 nm for the 3-Cl-py complex. The rate constants for quenching by water of the substituted complexes are as follows: $k_Q(H_2O) = 1.8 \times 10^7$ M^{-1} s^{-1} for $ReO_2(4\text{-}OMe\text{-}py)_4^+$ and $k_Q(H_2O) = 4.2 \times 10^5$ M^{-1} s^{-1} for $ReO_2(3\text{-}Cl\text{-}py)_4^+$. The rate constants increase in the order k_Q(3-Cl-py) < k_Q(py) < k_Q(4-OMe-py), which follows the pK_a's of the

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(10) Complex **1** was prepared by published procedures.[3] Quenchers were purchased from Aldrich and used as received except for 1,4-dihydro-4-imino-1-methylpyrimidine hydroiodide, which was prepared by a published procedure.[13] Emission spectra were recorded on a SPEX Fluoromax spectrometer and corrected for spectrometer response. For **1**, the emission maximum was 658 nm in all of the quenching experiments. Stern–Volmer plots were all linear with at least five measured points and $R \geq 0.99$. Samples were excited at 450 nm, and the emission maximum remained at 658 nm in all of the experiments. The k_Q for H_2O determined in this work was in good agreement with that determined by Winkler and Gray using lifetime quenching.[2]

(11) Stern–Volmer quenching by benzoic acid of electronically related ReN^{2+} excited states in acetonitrile has been observed: Bakir, M.; Sullivan, B. P. Unpublished results. Neyhart, G. A.; Seward, K. J.; Boaz, J.; Sullivan, B. P. *Inorg. Chem.* **1991,** *30,* 4488.

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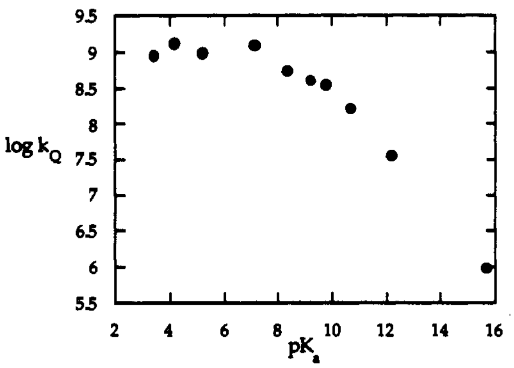

Figure 1. Plot of log k_Q for Stern–Volmer quenching of the excited state of $[ReO_2(py)_4]PF_6$ versus quencher pK_a.

protonated metal complexes. Again, these observations point to excited-state proton transfer as the deactivation mechanism.

The effect of deuteration of the acid is also consistent with a proton-transfer deactivation mechanism. Winkler and Gray have observed an isotope effect for H_2O/D_2O of $k_H/k_D = 8.6$,[2] a value that was also observed in aqueous micelles.[6] We have observed that the rate constant for quenching by ND_4^+ is 2.0×10^8 M^{-1} s^{-1}, giving an isotope effect for NH_4^+ of $k_H/k_D = 1.95$. The exact dependence of the isotope effect on the nature of the quencher remains to be determined; however, the existence of a substantial kinetic isotope effect is supportive of the proton-transfer mechanism. The isotope effect for NH_4^+ may be lower than that of water because NH_4^+ is in the diffusion-limited region in Figure 1.

A final point of interest involves the effect of solvent on the quenching rate. In Figure 1, the rate shows a relatively smooth dependence on the aqueous pK_a; however, the measurements were performed in acetonitrile. Values for pK_a's in acetonitrile do not show the same smooth trend. We have investigated the dependence of the quenching rate constants in Figure 1 as a function of solvent. We find that changing the solvent from acetonitrile to nitromethane, dimethyl sulfoxide, or acetone has no quantitative effect on the results in Figure 1. The only variation we have seen with solvent appears with less polar chlorinated solvents, such as dichloromethane or chloroform, which lead to a loss of curvature in the plot, consistent with a larger intrinsic barrier to proton transfer.[21,22] Thus, the thermodynamic picture may be somewhat different in these low-dielectric solvents.

As a preliminary model, we propose that proton transfer occurs within a hydrogen-bonded pair where the acidic proton is associated with an oxo ligand, for which there is evidence from NMR studies.[3] Within this pair, there may be little involvement of the solvent, and the aqueous pK_a may be the best measure of the thermodynamics of proton transfer within the solvated, hydrogen-bonded pair. At the moment, important questions remain regarding the static or transient nature of the hydrogen-bonded adduct and the effect of the adduct on the kinetic analysis. Experiments using metal–hydride acid quenchers, which do not form hydrogen bonds,[23] are underway. Nevertheless, it appears that proton transfer is indeed the quenching mechanism, and further experimentation will elucidate the precise events occurring in the excited-state deactivation process.

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