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Quantum Effects of High-Frequency Modes in Inorganic Electron Transfer: Kinetic Isotope Effects in Redox Reactions of $[Fe(H_2O)_6]^{2+}$, $[Fe(D_2O)_6]^{2+}$, and $Fe[(^{18}OH_2)_6]^{2+}$

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Abstract: Kinetic isotope effects have been measured for redox reactions of $Fe(H_2O)_6^{2+}$, $Fe(D_2O)_6^{2+}$, and $Fe(^{18}OH_2)_6^{2+}$ with a series of $M^{III}(bpy)_3$ oxidants ($M = Fe^{III}, Ru^{III}, Cr^{III}$). The rate ratios $k(^{16}OH_2)/k(^{18}OH_2)$ are well predicted by the recent treatment of Buhks, Bixon, and Jortner (*J. Phys. Chem.*, **85**, 3763 (1981)). Deuterium isotope effect measurements are complicated by the difference of the $Fe(aq)^{2+/3+}$ reduction potential in H_2O and D_2O: $E^0{}_{Fe^{3+}/H_2O} - E^0{}_{Fe^{3+}/D_2O} = -0.040$ V. After correcting the observed rates for the change in reaction driving force, an isotope effect of 1.3 is estimated for cross reactions involving $Fe(aq)^{2+/3+}$ (at $\Delta E = 0$). This value is larger than predicted and ~20% greater than that observed in the $^{16}OH_2$ vs. $^{18}OH_2$ experiments, possibly reflecting a contribution of "frozen" O–H modes in the reaction coordinate. Similarly, N–H modes may be involved to some extent in reductions of $Co(NH_3)_6^{3+}$.

In the early 1960's, a number of studies of isotope effects in inorganic electron-transfer rates appeared.[1] These studies subsequently waned, since no appropriate theory was available to guide the design and interpretation of such experiments. However, growing interest in quantum mechanical effects (e.g., nuclear tunneling) in electron-transfer reactions[2] has stimulated a search for experimental probes of quantum effects. Recently, Buhks et al. noted that kinetic isotope effects can in principle provide a probe of quantum effects in electron transfer at room temperature, and they obtained explicit expressions to predict such effects.[3] This treatment of KIE (kinetic isotope effects) is based on nonadiabatic multiphonon quantum mechanical theory of electron transfer in solution which presents the electron-transfer transition probability as a product of electronic interaction and Franck–Condon factors for nuclear vibrational modes. The key point in this analysis is that for many redox reactions, particularly of transition metals, quantum effects can arise when high-frequency (metal–ligand) modes (with frequency $\hbar\omega > kT$) undergo distortion during an electron-transfer reaction.

Consider, for example, the outer-sphere oxidation of $Fe(H_2O)_6^{2+}$. On oxidizing $Fe^{2+}(aq)$, the Fe–O bond lengths must decrease by ca. 0.15 Å (vide infra). This nuclear reorganization necessarily precedes electron transfer.[2,15] In many cases, this reorganization occurs by vibrational excitation of the appropriate mode (e.g., Fe–O symmetric stretch, $\hbar\omega \simeq 400$ cm^{-1}). However, when $\hbar\omega \geq kT$ the vibrational mode which allows nuclear reorganization cannot be fully populated by thermal excitation. Therefore, the electron-transfer reaction must occur (to some extent) by nuclear tunneling (i.e., tunneling through the barrier separating the diabatic potential surfaces in the space of nuclear coordinates). A pictorial representation of these concepts can be found in ref 2c. Since this quantum effect depends on the metal–ligand frequency $\hbar\omega$, it can be modulated by changing this frequency by isotopic substitution. It follows that kinetic isotope effects should be observed in outer-sphere electron-transfer reactions that involve substantial inner-sphere reorganization. Well-known examples include redox reactions involving $Fe(H_2O)_6^{2+}$ and $Co(NH_3)_6^{3+}$. Initial attempts to fit the best available experimental data on kinetic isotope effects with quantum mechanical theories seem disappointing.[3]

For the reactions

$$Co(NH_3)_6^{3+} + Cr(bpy)_3^{2+} \rightarrow Co(NH_3)_6^{2+} + Cr(bpy)_3^{3+} \quad \text{(Ia)}$$

$$Co(ND_3)_6^{3+} + Cr(bpy)_3^{2+} \rightarrow Co(ND_3)_6^{2+} + Cr(bpy)_3^{3+} \quad \text{(Ib)}$$

a deuterium isotope effect $(k_H/k_D)_{pred} = 1.12$ is predicted, while the observed effect is $(k_H/k_D)_{obsd} = 1.35$.[2,5] The calculations correspond to the model where the kinetic isotope effect is due to a change of the metal–ligand vibrational frequency upon substitution of H by D. However, several explicit predictions of theory remain untested. Chief among these is the suggestion that the isotope effect should decrease as the reaction driving force (ΔE) increases.

Finally, experiments have been complicated by the effect of solvent deuteration on redox potentials of many reactants. Weaver[6] has suggested that most observed deuterium isotope effects could be accounted for in part by this difference.

In order to clarify all these points, we have studied kinetic isotope effects in the electron-transfer reactions of $Fe^{II}(OH_2)_6^{2+}$, $Fe^{II}(OD_2)_6^{2+}$, and $Fe^{II}(^{18}OH_2)_6^{2+}$. An explicit correction for deuterium solvent isotope effects on the thermodynamic driving force is introduced. Three major conclusions emerge from this work as detailed below.

(1) Theory semiquantitatively predicts the kinetic isotope effect for substitution of $^{16}OH_2$ by $^{18}OH_2$ in the reaction $Cr(bpy)_3^{3+*} + [Fe(OH_2)_6]^{2+} \rightarrow Fe(OH_2)_6^{3+} + Cr(bpy)_3^{2+}$. (2) Theory correctly predicts a decrease in the kinetic isotope effect as the reaction driving force increases. (3) The observed isotope effect for replacement of H_2O by D_2O is significantly larger than predicted even after correcting for the solvent dependence of reaction driving force.

In conjunction with data for analogous Co^{III} systems, the results suggest that high-frequency O–H (or N–H) modes, which remain "frozen" during electron transfer, may dominate H/D isotope

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(1) (a) A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960). (b) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). (c) J. Hudis and R. W. Dodson, *ibid.*, **78**, 911 (1956). (d) J. Halpern, *Q. Rev., Chem. Soc.*, **15**, 207 (1961).

(2) (a) J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3640 (1974). (b) P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, **103**, 741 (1981). (c) B. S. Brunschwig, J. Logan, M. D. Newton, and N. Sutin, *ibid.*, **102**, 5798 (1980). (d) E. Buhks, M. Bixon, J. Jortner, and G. Navon, *J. Phys. Chem.*, **85**, 3763 (1981).

(3) E. Buhks, M. Bixon, and J. Jortner, *J. Phys. Chem.*, **85**, 3763 (1981).

(4) D. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

(5) (a) T. Guarr and G. McLendon, to be submitted for publication. (b) Y. Narusawa, M. Kimura, and K. Nakano, *Bull. Chem. Soc. Jpn.*, **47**, 2017 (1974). (c) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964). (d) G. M. Waind and R. Murray, *Proc. Int. Conf. Coord. Chem., 7th*, 309 (1962).

(6) (a) M. J. Weaver and S. M. Nettles, *Inorg. Chem.*, **19**, 1641 (1980). (b) E. Yee, R. Cave, K. Guyer, P. Tyma, and M. Weaver, *J. Am. Chem. Soc.*, **101**, 132 (1979). (c) M. Weaver, *Isr. J. Chem.*, **18**, 35 (1979). (d) M. Weaver, P. Tyma, and S. Nettles, *J. Electroanal. Chem. Interfacial Electrochem.*, **114**, 53 (1980).

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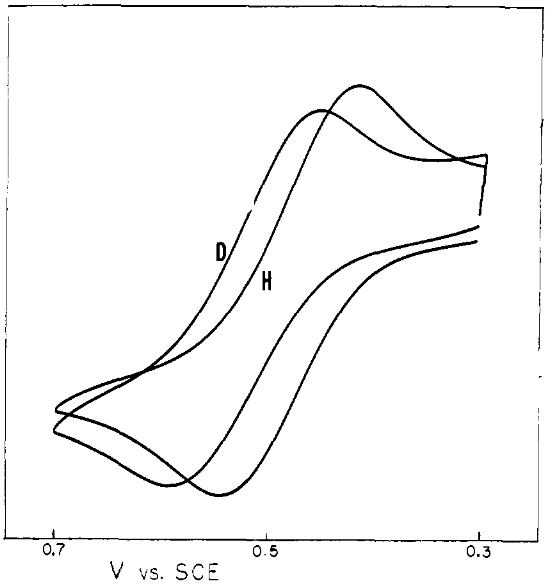

Figure 1. Cyclic voltammograms of Fe^{2+}(aq) in $^{16}H_2O$ and D_2O. Polished Pt disk working electrode, 25 °C, 0.16 M $NaClO_4$ and 0.04 M $HClO_4$; scan speed 20 mV/s.

effects and affect the rates of electron transfer.[18]

Materials and Methods

Materials. Ferrous ammonium sulfate (Baker) was recrystallized from water.

$Fe(bpy)_3^{3+}$, $Fe(4,4'\text{-}Me_2bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ [bpy = bipyridine; phen = phenanthroline] were prepared by addition of a stoichiometric amount of the ligand to Fe^{II} solutions in 0.1 M H_2SO_4, oxidation by lead dioxide, and crystallization of the Fe^{III} products as perchlorate salts by slow addition of $LiClO_4$ and cooling. $Ru(bpy)_3^{2+}$ (G. F. Smith Chem) was oxidized as above and isolated as the perchlorate salt. $Cr(bpy)_3^{3+}$, $Cr(4,7\text{-}Me_2phen)_3^{3+}$, and $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$ were prepared by addition of anhydrous $CrCl_2$ (or electrolytically reduced Cr^{II}) to a degassed aqueous suspension of the ligands.[7] After 5 min of stirring under N_2, the solutions were oxidized by bubbling with O_2. Excess Cr^{III} was filtered off, and excess ligand removed by adjusting the solutions to pH >7 and filtering, or by repeated extractions with 2-pentanone. The yellow aqueous layer was concentrated on a rotovap and chilled, whereon analytically pure yellow crystals separated. All the metal(III) bipyridyl and phenanthroline complexes were stored dessicated and frozen until use. They were dissolved in 0.04 M H_2SO_4 solution within 30 min of use and were rigorously protected from light.

D_2O was obtained from Aldrich and was 99.8% D.

H_2O was doubly glass distilled.

$H_2{}^{18}O$ was obtained from Stohler Isotopes. Purity was >98% ^{18}O and >98% ^1H.

Stopped-flow measurements were made on a Durrum D-110 stopped flow equipped with dual detection and interfaced to a PDP 11/45. All reactions were repeated 3–4 times and then repeated with different preparations of Fe^{2+} and the oxidants.

Emission quenching measurements were made in a Perkin-Elmer MPF-44A spectrofluorimeter. Small aliquots (<10 μL) of degassed Fe^{2+} solutions in 0.04 M H_2SO_4 were added by a gas-tight microliter syringe to N_2-saturated solutions of the Cr complexes. A small volume fluorescence cell (volume < 0.5 mL) was used. Mixing was ensured by repeated inversion or with an agitation mixer. Some experiments were also carried out in air. No difference was found in the observed *isotope* effect between air-saturated and N_2-saturated experiments. Experiments were repeated in triplicate with individually prepared reagents for each run. Precision of better than 1% was observed in the best case, using $Cr(Me_2phen)_3^{3+}$ as the electron acceptor. The data were analyzed by a standard Stern–Volmer procedure, plotting I_0/I vs. $[Fe^{2+}]$. k_H/k_D and k_{16}/k_{18} were obtained from the ratio of the slopes of the Stern–Volmer plots.

Electrochemical (cyclic voltammetry) measurements were made on a PAR electrochemistry system consisting of a Model 173 potentiostat galvanostat and a Model 175 universal programmer (waveform generator). A three-electrode system was used which included a freshly polished Pt disk (or glassy carbon) working electrode, an Ag|AgCl or calomel reference electrode, and a Pt (spiral) auxiliary electrode. The three electrodes were held in fixed, reproducible positions by the design of the cell top. Individual cyclic voltammetry experiments were repeated with several different preparations of Fe^{2+}(aq). Cathodic peak–anodic peak separations (E_{pp}) at a given scan rate were reproducible to ≤5%. Solutions were N_2 scrubbed and an N_2 blanket was maintained over the solutions.

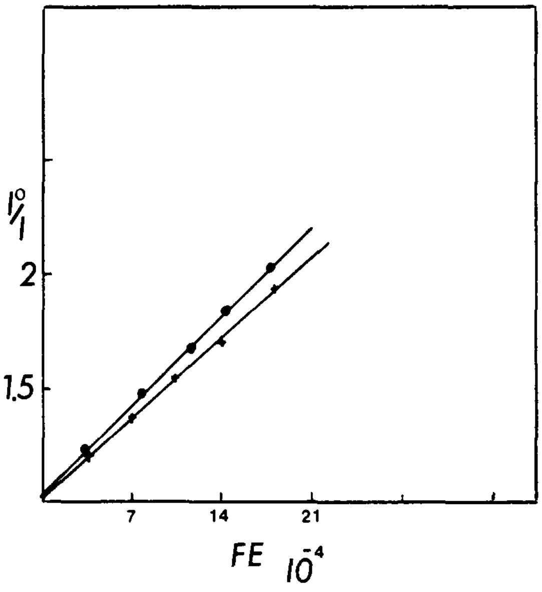

Figure 2. Stern–Volmer quenching of $Cr(4,7\text{-}Me_2phen)_3^{3+}$ by Fe^{2+}. Stern–Volmer quenching of ^2E $Cr(4,7\text{-}Me_2phen)_3^{3+}$ by Fe^{2+} in $^{16}OH_2$ (upper line) and $^{18}OH_2$ (lower line).

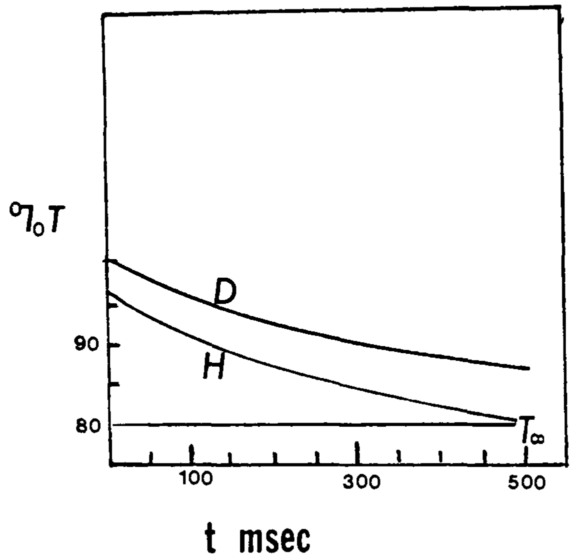

Figure 3. Stopped-flow kinetics traces of the oxidation of Fe^{2+} by $Fe(4,4'\text{-}Me_2bpy)_3^{3+}$ in H_2O and D_2O (0.01 M H_2SO_4).

Results and Discussion

Redox Potentials. Since $Fe(aq)^{2+/3+}$ formal potentials are somewhat medium dependent, redox potentials were determined for all reagents used in these studies, in 0.04 M $HClO_4$ and 0.16 M $NaClO_4$. Cyclic voltammograms for $Fe(aq)^{2+/3+}$ in H_2O, D_2O, and $^{18}OH_2$ are shown in Figures 1 and 4. The oxidation potential of $Fe(aq)^{2+/3+}$ in D_2O ($E^0_{D_2O} = 0.76$) is greater than that in H_2O ($E^0_{H_2O} \simeq 0.72$) by 0.040 V. This difference agrees precisely with the previous report by Weaver.[6a] Elegant studies by Weaver's group have suggested that this solvent dependence of the reduction potential partly reflects different solvation entropies in D_2O and H_2O. The original papers[6] should be consulted for details. In D_2O, the observed cyclic voltammograms are only quasireversible[17] ($E_{pp} \geq 80$ mV) even at scan rates of 10 mV/s, while the cyclic

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[7] (a) D. Miller, Ph.D. Thesis, University of Rochester, 1981. (b) B. R. Baker and B. D. Mehta, *Inorg. Chem.*, **4**, 848 (1965).

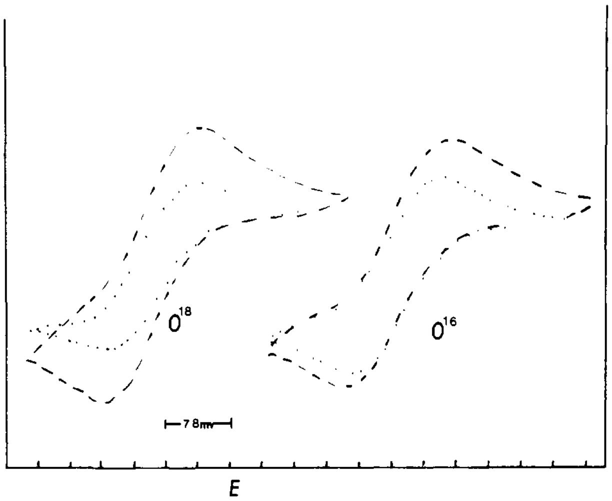

Figure 4. Cyclic voltammograms of Fe^{2+}(aq) in $^{16}OH_2$ and $^{18}OH_2$, same conditions as Figure 1. Scan speed = 5 (···) and 20 mV/s (---).

Table I. Redox Potentials[a] for $M^{III}(bpy)_3{}^{3+}$ Homologues

complex	E^0(3+/2+), V	$^*E^0(M^{*3+}/M^{2+})$, V
$Cr(bpy)_3{}^{3+}$	−0.24	1.46
$Cr(Me_2bpy)_3{}^{3+}$	−0.40	1.31
$Cr(Me_2phen)_3{}^{3+}$	−0.44	1.26
$Cr(Me_4phen)_3{}^{3+}$	−0.57	1.10
$Fe(bpy)_3{}^{3+}$	1.07	
$Fe(Me_2bpy)_3{}^{3+}$	0.92	
$Fe(phen)_3{}^{3+}$	1.10	
$Fe(Me_2phen)_3{}^{3+}$	0.94	
$Ru(bpy)_3{}^{3+}$	1.26	

[a] 25 °C, E^0 vs. NHE, 0.1 M KNO_3, 0.01 M H_2SO_4.

voltammogram in H_2O is more nearly reversible. The observed $Fe(aq)^{2+/3+}$ oxidation potentials in $^{16}OH_2$ and $^{18}OH_2$ are *identical* within experimental error (±5 mV).

Reversible cyclic voltammograms ($E^0_{pp} < 80$ mV) were obtained under corresponding conditions for all the M^{III}bpy systems (M = Fe^{III}, Cr^{III}, Ru^{III}).[17] The results are in good agreement with previous literature values.[8] All the observed electrochemical measurements are summarized in Table I.

$^{16}OH_2/^{18}OH_2$ Kinetic Isotope Effects on Excited-State Electron-Transfer Quenching. Small kinetic isotope effects on electron-transfer rates ($k_{16}/k_{18} = 1.06 \pm 0.01$, see below) are predicted when $^{18}OH_2$ replaces $^{16}OH_2$ in $Fe(aq)^{2+}$. We therefore sought a very precise kinetic method that requires reasonably small quantities of $^{18}OH_2$. A good method is provided by measuring excited-state quenching reactions.

$$Cr(LL)_3{}^{3+*} + Fe(OH_2)_6{}^{2+} \rightarrow Cr(LL)_3{}^{2+} + Fe(OH_2)_6{}^{3+}$$

LL = bipyridine, 4,7-dimethylphenanthroline,
or 3,4,7,8-tetramethylphenanthroline

These reactions have been studied in great detail by Hoffman,[9] Sutin,[10] and others.[11] Flash experiments,[9,10] reproduced in this work, showed that all emission quenching was due to electron transfer, and not energy transfer. Therefore, precise kinetic data can be obtained by measurement of quenching of ^2E Cr emission intensity by Fe^{2+} (i.e., Stern–Volmer quenching). Stern–Volmer plots are shown in Figure 2 for quenching of ^2E $Cr(4,7\text{-}Me_2phen)_3{}^{3+}$ by Fe^{2+} in $^{16}OH_2$ and $^{18}OH_2$. A small but very reproducible kinetic isotope effect is found, $k_{16}/k_{18} = 1.08 \pm 0.01$.

Table II. Kinetic Isotope Effects for Outer-Sphere Redox Reactions of Hexaaquo Fe^{II}

reaction	ΔE_H	$(k_H/k_D)_{obsd}$	$(k_H/k_D)_{corr}{}^a$	k_{16}/k_{18}
$Fe(Me_2bpy)_3{}^{3+} + Fe^{II}$	0.15	2.5 ± 0.1	1.22	
$Fe(phen)_3{}^{3+} + Fe^{II}$	0.30	2.2 ± 0.1	1.17	
$Ru(bpy)_3{}^{3+} + Fe^{II}$	0.56	1.8 ± 0.1	1.09	
$Cr(Me_4phen)_3{}^{3+*} + Fe^{II}$	0.35			1.09 ± 0.02
$Cr(Me_2phen)_3{}^{3+*} + Fe^{II}$	0.50	1.75 ± 0.1	1.03	1.08 ± 0.01
$Cr(bpy)_3{}^{3+*} + Fe^{II}$	0.75	1.6 ± 0.1	1.07	1.04 ± 0.01
$Ru(bpy)_3{}^{2+*} + Fe^{III}$	1.5			1.0

[a] k_H/k_D, corrected for the potential difference with use of the equation $\ln(k_H/k_D) = ([\Delta E_D - \Delta E_H]/2kT)([\Delta E_H/E_r] - 1)$ with $E_r = 1.5$ V and $\Delta E_D - \Delta E_H = 0.04$ V. This equation is strictly valid only when $\Delta E_H = 0$ or $\Delta E_H = E_r$ (see text). Thus $(k_H/k_D)_{corr}$ cannot be readily compared with k_{16}/k_{18} at intermediate ΔE_H values.

This reaction has a net driving force $\Delta E = E_{^2ECr^{3+*}} + E^0{}_{Cr^{3+}} - E^0{}_{Fe^{3+}} = 0.5$ V. To test the dependence of the kinetic isotope effect on ΔE, corresponding data were obtained for Fe^{2+} quenching of $Cr(Me_4phen)_3{}^{3+}$ ($\Delta E = 0.40$ V) and $Cr(bpy)_3{}^{3+}$ ($\Delta E = 0.75$ V). The quenching data were far less precise for $Cr(Me_4phen)_3{}^{3+*}$, due in part to the limited solubility of this complex: $k_{16}/k_{18} = 1.10 \pm 0.05$. For Fe^{II} quenching of $Cr(bpy)_3{}^{3+*}$, a quite small but reproducible effect was obtained, $k_{16}/k_{18} = 1.035 \pm 0.005$.

Qualitatively, at least, these data do support the theoretical prediction[3] that the kinetic isotope effect decreases as ΔE increases. The limited number of data preclude a rigorous quantitative analysis. The theoretical analysis[3] of the Frank–Condon factors predicts the largest isotope effect in the "normal" region for $\Delta E = 0$, as given by the following expression, accounting for metal–ligand vibrational modes:

$$k_{16}/k_{18} = \exp[Y_{^{18}O} - Y_{^{16}O}] \tag{1}$$

where

$$Y = 2(\Delta d)^2\omega'\omega''[\omega' \coth \nu'' + \omega'' \coth \nu']^{-1} \tag{2}$$

$$\nu' = \hbar\omega'/4kT \qquad \nu'' = \hbar\omega''/4kT \tag{3}$$

and Δd is the reduced displacement

$$(\Delta d)^2 = 6(\Delta r_{Fe\text{-}O})^2 m/\hbar \tag{4}$$

which is determined by a change in metal–ligand distance, $\Delta r_{Fe\text{-}O}$, due to electron-transfer reaction, and by a ligand mass m, which is changed isotopically in our study. ω' and ω'' designate the totally symmetric vibrational metal–ligand frequencies in $Fe^{3+}(\omega')$ and $Fe^{2+}(\omega'')$ oxidation states of iron. The change of these frequencies upon isotopic substitution of oxygen is given by $\omega(^{18}OH_2) = \omega(^{16}OH_2)(18/20)^{1/2}$. Thus, if $\hbar\omega' = 490$ cm^{-1} and $\hbar\omega'' = 390$ cm^{-1} for $Fe(^{16}OH_2)_6{}^{3+}$ and $Fe(^{16}OH_2)_6{}^{2+}$, respectively,[12] $\hbar\omega' = 465$ cm^{-1} and $\hbar\omega'' = 370$ cm^{-1} for $Fe(^{18}OH_2)_6{}^{3+,2+}$. Equation 1 is derived for a self-exchange reaction between a pair of ions. In considering only an oxidation (or reduction) half-reaction (at $\Delta E = 0$), Y is reduced by a factor of 2.

If one takes the recent estimate[13] of 0.14 Å for the difference (Δr) in iron–oxygen bond lengths in $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$, the $^{16}OH_2/^{18}OH_2$ kinetic isotope effect for the Fe^{2+}/Fe^{3+} self-exchange reaction in aqueous media is predicted to be 1.10 (eq 1), while for the oxidation half-reaction only, $(k_{16}/k_{18})_{pred} = 1.05$ at $\Delta E = 0$. When a different experimental estimate of the difference in Fe–O bond lengths is used,[14] $\Delta r = 0.17$ Å, eq 1 predicts $k_{16}/k_{18} = 1.14$ for the same self-exchange reaction and 1.07 for the oxidation of $Fe(OH_2)_6{}^{2+}$ at $\Delta E = 0$. An average metal–ligand frequency for $Fe(^{16}OH_2)_6{}^{2+/3+}$ is $\hbar\omega = 440$

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

(9) N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta, and M. Maestri, *J. Am. Chem. Soc.*, **101**, 2907 (1979).

(10) B. Brunschwig and N. Sutin, *J. Am. Chem. Soc.*, **100**, 7568 (1978).

(11) N. Serpone, *Coord. Chem. Rev.*, **39**, 121 (1981).

(12) J. Nagakawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

(13) N. J. Hair and J. K. Beattie, *Inorg. Chem.*, **16**, 245 (1977).

(14) (a) D. W. Clark and M. S. Farrinmod, *J. Chem. Soc. A*, 299 (1971). (b) M. T. Barnet, B. M. Graven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

(15) (a) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965). (b) N. Sutin in "Inorganic Biochemistry", C. Eichorn, Ed., Elsevier, NY 1974.

(16) K. Frese, *J. Phys. Chem.*, **85**, 3911 (1981).

cm^{-1}. The electron-phonon coupling parameter $S = 1/2(\Delta d)^2\hbar\omega = 13.9$ and the reorganization energy of metal-ligand vibrational modes for oxidation of $Fe(^{16}OH_2)_6^{2+}$ $E_c = S\hbar\omega \approx 0.8$ V. Our preliminary experimental observations indicate that k_{16}/k_{18} is reduced to unity for $\Delta E = +1.5$ V (Table II). The isotope effect should vanish when $\Delta E = E_r = E_s + E_c$. Thus, with $E_r = 1.5$ V and $E_c = 0.8$ V solvent-reorganization energy is estimated as $E_s \simeq 0.7$ V. Using these values, one can estimate the dependence of k_{16}/k_{18} on driving force ΔE from Figure 2 of ref 3 which was derived for the similar effect in hexaamine complexes. This treatment predicts a decrease in the isotope effect from $k_{16}/k_{18} = 1.07$ at $\Delta E = 0$, to $k_{16}/k_{18} = 1.05$ at $\Delta E = 0.5$ V, to $k_{16}/k_{18} = 1.03$ at $\Delta E = 0.75$ V. These predicted isotope effects are in reasonable qualitative and semiquantitative agreement with experiment (cf. Table II).

In summary, the $^{16}OH_2/^{18}OH_2$ isotope effect measurements confirm both the qualitative and semiquantitative predictions of a quantum mechanical treatment[3] of $Fe(OH_2)_6^{2+}$ electron-transfer reactions. These results suggest that theory has properly treated the principal effect of isotopic substitution, and consequent changes in $\hbar\omega$ and nuclear tunneling probability.

Why then does the theory fail to predict the H/D isotope effects for the reduction of $Co(NH_3)_6^{3+}$ and $Co(ND_3)_6^{3+}$? Are reactions of Co^{III} somehow anomalous, or does deuterium substitution change more than just the metal-ligand stretching frequency?

To attempt to answer these questions, we next compare the electron-transfer rates of $Fe(OH_2)_6^{2+}$ and $Fe(OD_2)_6^{2+}$.

H-D Kinetic Isotope Effects. Very large changes in rate are observed in electron-transfer cross reactions of Fe^{2+}(aq) in D_2O solution vs. H_2O solution. For the cross reaction with $Fe(4,4'\text{-}Me_2bpy)_3^{3+}$, $k_H/k_D \simeq 2.5$ (see Figure 3 and Table II).

However, as Weaver noted,[6] and is confirmed in this work, large values of k_H/k_D may simply reflect the difference in redox potentials (0.04 V) between $Fe(aq)^{2+}$ in H_2O and D_2O.[17] For a classical reaction path, in the high-temperature approximation electron transfer depends parabolically on the driving force. Using the classical (Marcus) expression[15] provides a correction for this solvent effect on ΔE, as outlined below.

Let

$$k_H \sim \exp\{-[(\Delta E_H - E_r)^2/4kTE_r]\} \quad (5)$$

and

$$k_D \sim \exp\{-[(\Delta E_D - E_r)^2/4kTE_r]\} \quad (6)$$

$$\ln (k_H/k_D) = (\epsilon/2kT)[\Delta E_H/E_r - 1] \quad (7)$$

where $\epsilon = \Delta E_D - \Delta E_H < 0$ and $\epsilon/2E_r \ll 1$.

For the cross reactions of Fe^{2+}(aq) with $M^{III}(bpy)_3^{3+}$, E_r has been carefully estimated[16] as $E_r = 1.5$ V. Taking $\epsilon = -0.04$ V, eq 7 gives a maximum correction of $k_H/k_D = 2.1$ at $\Delta E_H = 0$ V. This equation has been used to correct the observed values of k_H/k_D for driving force, as summarized in Table II.

It may be noteworthy that the "corrected" electron-transfer isotope effect so calculated ($k_H/k_D \sim 1.2$) approaches the value for $Co(NH_3)_6^{3+}$ which undergoes similar reorganization during electron transfer.[4] For the cobalt(III) reactions, the solvent isotope effect is small.[3,4] Therefore, even allowing for some uncertainty in the correction factor, it seems clear that the (corrected) kinetic isotope effect on substituting H_2O by D_2O is significantly larger than on substituting $^{16}OH_2$ by $^{18}OH_2$. This is not expected, since the mass difference ($^{18}OH_2 - {}^{16}OH_2$) = ($^{16}OD_2 - {}^{16}OH_2$) = 2. Thus a nearly identical shift in the symmetric metal-ligand stretching frequency should occur for substitution of $^{16}OH_2$ by $^{16}OD_2$ *or* by $^{18}OH_2$.

The most obvious explanation is that deuterium substitution in $Fe(OH_2)_6^{2+}/Fe(OD_2)_6^{2+}$ or in $Co(NH_3)_6^{3+}/Co(ND_3)_6^{3+}$ not only affects metal-ligand modes but may also affect high-frequency O-H (or N-H) modes that undergo small displacements when the metal oxidation state changes. Since O-H and N-H modes occur at very high frequency (e.g., ν_{O-H} stretch $\sim$3600 cm^{-1}), these modes would remain "frozen" during electron transfer, and electron transfer would necessarily proceed (in the O-H coordinate) by nuclear tunneling.

For illustrative purposes, the effect of a small oxidation-state-dependent change in an O-H bond may be considered. For the purpose of this treatment, an oxidation-state-dependent change in an O-H bond might directly involve a bound ligand, or the effect may arise in the second solvation shell. If changes in the average bonding of the second shell were involved, the number of oscillators would increase, and Δr would decrease. The contribution of this "frozen" O-H mode to the isotope effect on the electron-transfer half-reaction at $\Delta E = 0$ is given by the low-temperature approximation[3] ($\hbar\omega_{O-H} \ll kT$):

$$\ln (k_{O-H}/k_{O-D}) = \frac{E_{O-H}}{\hbar\omega_{O-H}}\left[\left(\frac{m_D}{m_H}\right)^{1/2} - 1\right] = Y_{O-D} - Y_{O-H} \quad (8)$$

where

$$Y_{O-H} = \frac{E_{O-H}}{\hbar\omega_{O-H}} = S_{O-H} = 12m_H\omega_{O-H}(\Delta r_{O-H})^2/2\hbar \quad (9)$$

Using eq 8 and 9 one can estimate the coupling parameter $S_{O-H} = 0.5$, the reorganization energy for O-H modes $E_{O-H} = 0.2$ eV, and the change of O-H bond distance due to electron transfer $\Delta r_{O-H} = 0.03$ Å. These parameters will predict an isotope effect ratio $k_{O-H}/k_{O-D} = 1.25$ attributed to the vibrational frequency of $\omega_{O-H} = 3600$ cm^{-1}.

A detailed analysis of the deuterium isotope effect on the electron-transfer rate involves numerical solution of the saddle-point equation[3] and calculation of the Franck-Condon factors when ΔE, ω_{Fe-OH_2}, and ω_{O-H} are allowed to vary with isotopic substitution. In general, these three effects are mixed together. Using the classical approximation (eq 7) to correct k_H/k_D for the solvent dependence of driving force gives an error of $\sim$7% when $\Delta E \simeq E_r/2 \simeq 0.8$ V. The approximation is valid within experimental error (1%) for small ΔE ($\Delta E/E_r \leq 0.1$) and where ΔE is close to E_r ($1 - \Delta E/E_r \leq 0.1$). For electron-transfer processes at $\Delta E = 0$, all the contributing effects to k_H/k_D can be factored into the analytical form

$$k_H/k_D = \exp\left(\frac{\epsilon}{2kT}\right) \exp[Y_{Fe-OD_2} - Y_{Fe-OH_2}] \exp[Y_{O-D} - Y_{O-H}] \quad (10)$$

The second exponential in eq 10 can be estimated by measurement of the $^{16}OH_2/^{18}OH_2$ isotope effect on iron oxidation at $\Delta E = 0$. From extrapolation of the data in Table II, $k_H/k_D \simeq 2.8$ and $k_{16}/k_{18} \simeq 1.1$ at $\Delta E = 0$. The corrected value is $(k_H/k_D)_{corr} \simeq 1.3$ (at $\Delta E = 0$). Therefore, tunneling along the O-H vibration contributes a factor of $\sim$1.2 to the deuterium isotope effect. This extrapolation from experimental results is quite close to our estimation of 1.25 on the basis of eq 8.

The parameters thus estimated can provide an evaluation of the role of high-frequency O-H vibrational modes in electron-transfer processes in inorganic systems. The possible contribution of high-frequency O-H modes to the Franck-Condon factors (and rate) of electron transfer is of the order of $\exp[-Y_{O-H}] = \exp[-S_{O-H}] \simeq 0.5$ per half-reaction, or $(0.5)^2 = 0.25$ for the self-exchange. This is quite small compared with the contribution of metal-ligand vibrational modes ($\exp[-Y_{Fe-OH_2}] \simeq 1 \times 10^{-6}$ for self-exchange reactions of $Fe(OH_2)_6^{2+}/Fe(OH_2)_6^{3+}$). However, the high-frequency "frozen" O-H vibrational modes may dominate the kinetic isotope effect upon deuteration, giving $k_H/k_D = 1.2\text{-}1.3$ instead of the 1.05-1.1 expected when considering only metal-ligand vibrational modes.

Thus, studies of the kinetic isotope effects k_{16}/k_{18} and k_H/k_D may provide important information about the mechanism of electron-transfer processes.[18] It is clearly important to establish

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(17) It is assumed that the H/D solvent effect on the $M(bpy)_3^{(n+1)+/n+}$ couple is negligible. This assumption was confirmed in our lab and in ref 6.

(18) J. Bigeleisen, *J. Chem. Phys.*, **32**, 1583 (1960).

whether any O–H bond changes occur (using neutron diffraction, or perhaps ENDOR). At present, insufficient data are available to allow a structural comparison. Since theory satisfactorily accounts for the effect of $^{18}OH_2$ substitution, the "frozen mode" explanation seems an interesting possibility for explaining the large H/D isotope effects in electron-transfer reactions of $Co(NH_3)_6^{3+}/Co(ND_3)_6^{3+}$ and $Fe(OH_2)_6^{2+}/Fe(OD_2)_6^{2+}$. In any case, it seems clear that the kinetic isotope effect in $Fe^{2+/3+}$ redox reactions due to substitution of H_2O by D_2O is larger than that due to the substitution of $^{16}OH_2$ by $^{18}OH_2$. Since D_2O and $^{18}OH_2$ have an identical mass, this kinetic isotope effect $Fe^{2+/3+}(k_H/k_D)/Fe^{2+/3+}(k_{16}/k_{18}) > 1$ cannot be due to metal–ligand modes alone but incorporates the effect of the change in driving force and, possibly, the effect of "intraligand" vibrational modes.

Summary

Several conclusions can be drawn from the results pesented here.

(1) The effect on electron-transfer rates of substituting ligands of different mass, e.g., $[Fe(^{16}OH_2)_6]^{2+}/[Fe(^{18}OH_2)_6]^{2+}$, apparently can be understood by considering the effect of the mass change on the frequency ($\hbar\omega$) of the symmetric metal–ligand stretching mode. These results strongly support the recent quantum theories of electron transfer.[2,3] The specific treatment of Buhks et al.[3] also correctly predicts both the direction and magnitude of the dependence of the kinetic isotope on reaction driving force.

(2) By contrast, substitution of H by D in $Fe(OH_2)_6^{2+}/Fe(OD_2)_6^{2+}$ or $Co(NH_3)_6^{3+}/Co(ND_3)_6^{3+}$ causes a larger kinetic isotope effect than can be explained by the change in metal–ligand frequency. We wish to suggest that very high frequency (N–H) or (O–H) modes are involved (to a small extent) in electron-transfer reactions of some transition-metal complexes. Since these modes cannot be thermally populated, the reaction must involve nuclear tunneling. The small calculated changes in O–H (or N–H) bonds that are invoked to explain the isotope effect might involve the bound ligand directly, or may be coupled to second shell solvent.

These initial results suggest a number of further experiments. In particular, it will be interesting to seek further confirmation of "frozen mode" behavior in electron transfer. We are pursuing such studies in reactions of free and coordinated O_2. Temperature-dependence studies of the isotope effect at low temperatures may provide additional information about the tunneling mechanism of electron-transfer reactions.

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Registry No. D_2, 7782-39-0; ^{18}O, 14797-71-8; Fe, 7439-89-6; $Fe(Me_2bpy)_3^{3+}$, 34032-03-6; $Fe(phen)_3^{3+}$, 15276-16-1; $Ru(bpy)_3^{3+}$, 18955-01-6; $Cr(Me_4phen)_3^{3+}$, 51194-74-2; $Cr(Me_2phen)_3^{3+}$, 51194-72-0; $Cr(bpy)_3^{3+}$, 15276-15-0; $Ru(bpy)_3^{2+}$, 15158-62-0.

Solid-State NMR Studies of the Reactions of Silica Surfaces with Polyfunctional Chloromethylsilanes and Ethoxymethylsilanes

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Abstract: The silylation of silica surfaces by dimethyldichlorosilane, methyltrichlorosilane, dimethyldiethoxysilane, and methyltriethoxysilane has been studied by solid-state ^{29}Si and ^{13}C NMR, by use of cross polarization (CP) and magic-angle spinning (MAS). An earlier formalism for the quantitative analysis of the NMR data has been extended for use with polyfunctional silylating agents and applied in detail to dimethyldichlorosilane reactions. Silylation with ethoxysilane reagents is less amenable to quantitative interpretation but appears to parallel closely the behavior of analogous chlorosilane reagents. With ethoxysilane reagents ^{13}C NMR is found to be quite useful, especially for determining the fate of ethoxy groups. In all of the cases studied, the products are characterized primarily by single silane-to-surface attachments of each silane silicon atom. The presence of adsorbed water is found to play an important role in the course and rate of the silylation reactions, especially those employing ethoxysilane reagents. The NMR data are used to address the question of "horizontal" and "vertical" polymerization within the "silane phase" on the silica surface.

Introduction

Previous reports have described the use of solid-state ^{29}Si NMR, by use of cross polarization (CP)[1] and magic-angle spinning (MAS),[2] in the characterization of silica surfaces[3,4] and their derivitization by monofunctional silylating agents[5,6] (e.g., trimethylchlorosilane and hexamethyldisilizane). These reports have shown that ^{29}Si CP/MAS spectra of silica gels are amenable to quantitative analysis and have included formalisms for deriving chemically useful structural parameters from such analysis.

In many chemical applications, e.g., chromatographic phases and supported catalysts, silica surfaces are derivatized by silylating agents with more than one labile group, e.g., $R\text{-}Si(OEt)_3$ and $R\text{-}SiCl_3$. Such systems are potentially much more diverse in their silylation chemistry than monofunctional reagents. In addition to the single attachment to the surface that would result from

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(1) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 509.

(2) Andrew, E. R.; Eades, R. G. *Proc. R. Soc. London, Ser. A* **1953**, *216*, 398.

(3) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

(4) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.

(5) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208.

(6) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.*, in press.

0002-7863/83/1505-3767$01.50/0