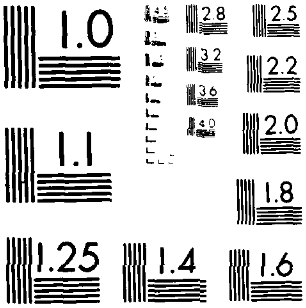
AD-A126 726 COMPARISONS BETWEEN THEORETICAL AND EXPERIMENTAL 1/1
DEUTERIUM ISOTOPE EFFECT..(U) PURDUE UNIV LAFAYETTE IN
DEPT OF CHEMISTRY M J WEAVER ET AL. MAR 83 TR-13
UNCLASSIFIED N00014-83-K-0086 F/G 7/4 NL

END
DATE
FILMED
[illegible] 83
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

②

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0086

TECHNICAL REPORT NO. 13

Comparisons between Theoretical and Experimental Deuterium Isotope Effects for Some Outer-Sphere Electrochemical Reactions

by

Michael J. Weaver and Tomi T.-T. Li

Prepared for Publication

in the

Journal of Physical Chemistry

Department of Chemistry
Purdue University
West Lafayette, IN 47907

March 1983

DTIC
ELECTE
APR 13 1983
S D
H

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 13	2. GOVT ACCESSION NO. AD-A126726	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Comparison between Theoretical and Experimental Deuterium Isotope Effects for Some Outer-Sphere Electrochemical Reactions		5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 13
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Michael J. Weaver and Tomi T.-T. Li		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0086
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Purdue University West Lafayette, IN 47907		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE March 1983
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Deuterium Isotope Effects, Outer-Sphere Electron Transfer, Nuclear Tunneling, Solvent Effects

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Experimental deuterium isotope effects upon the rates of outer-sphere electrochemical exchange reactions involving aquo and ammine complexes are compared with the predictions of comtemporary theories which take into account nuclear tunneling from inner-shell vibrational modes. The isotope rate ratios calculated by considering nuclear tunneling of metal-ligand vibrational modes are in most cases much smaller than the observed rate ratios. Significant additional contributions may arise from nuclear tunneling associated with internal ligand stretching modes, although this is estimated

DD FORM 1 JAN 73 1473

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

to be unlikely to account for the very large isotope effect observed for hexaaquochromium(III)/(II). The disparities seen between theory and experiment are speculated to be due to a contribution to the outer-shell reorganization energy from reorientation of hydrogen-bound solvent molecules. This conclusion is supported by the marked disparities seen between the relative isotope rate ratios for corresponding electrochemical and homogeneous reactions in comparison with the predictions of the dielectric continuum model.

We have recently found that significant and even substantial rate decreases occur for a number of one-electron electrochemical reactions involving aquo and ammine complexes at the mercury-water interface upon replacing the aqueous solvent with D_2O.[1] Such solvent isotope effects may arise from differences in the interactions between the complex and the surrounding solvent as well as from changes in the inner-shell barrier to electron transfer due to replacement of hydrogen by deuterium in the reactant coordination sphere ("primary" isotope effect).[1,2] The observed isotope effects are much larger than those predicted by the classical model of outer-sphere electron transfer. This treats the inner-shell (metal-ligand) contribution to the Franck-Condon barrier in terms of a harmonic oscillator, and the outer-shell (solvent repolarization) component by using the dielectric continuum approximation.[3] Moreover, even the relative isotope rate ratios for outer-sphere electrochemical and homogeneous reactions involving the same redox couples were found to differ substantially from the predictions of this model.[1] It was speculated that the observed electrochemical isotope effects are associated chiefly with differences in the extent of ligand-solvent hydrogen bonding in D_2O and H_2O.[1]

It has recently been pointed out that contemporary models of electron transfer which provide a quantum-mechanical description of inner-shell reorganization[4-6] predict significant primary isotope effects for systems with large inner-shell barriers. These effects arise from the decrease in the degree of nuclear tunneling when the ligands are deuterated.[7,8] In principle, the comparison of experimental isotope effects with these theoretical predictions should provide a sensitive test of the applicability of such models for describing the inner-shell vibrational modes. Such a comparison for the electrochemical kinetic isotope effects reported in ref. 1 is given in the present communication. The findings implicate the importance of hydrogen bonding between the inner-shell ligands and surrounding water molecules to the electron-transfer energetics.

Aquo Redox Couples

Table I contains a summary of the observed rate ratios for electrochemical exchange $(k^H_{ex}/k^D_{ex})_{ob}$, (i.e. ratios of "standard" rate constants) for $Fe^{3+/2+}_{aq}$, $V^{3+/2+}_{aq}$, $Cr^{3+/2+}_{aq}$, and $Eu^{3+/2+}_{aq}$ (where "aq" represents aquo ligands) at mercury electrodes upon replacing H_2O with D_2O solvent. These rate ratios are taken from ref. 1; they are corrected for electrostatic double-layer effects.[1] The uniform finding that $(k^H_{ex}/k^D_{ex})_{ob} > 1$ indicates that ligand and/or solvent deuteration yields significant increases in the intrinsic electrochemical barriers; i.e. in the activation free energy in the absence of an electrochemical driving force. Listed for comparison in Table 1 are calculated values of k^H_{ex}/k^D_{ex}, $(k^H_{ex}/k^D_{ex})_{calc}$, obtained from a "semiclassical" treatment of outer-sphere electron transfer[4] using the relation[9]

$$(k^H_{ex}/k^D_{ex})_{calc} = (\nu^H_n/\nu^D_n)\ \exp\{[\Delta G^*_{in}(T)_D - \Delta G^*_{in}(T)_H]/RT\}.$$

$$\exp\{[(\Delta G^*_{out})_D - (\Delta G^*_{out})_H]/RT\} \qquad (1a)$$

$$= (\nu^H_n/\nu^D_n)\ (k^H/k^D)_{out}\ (\Gamma^H_n/\Gamma^D_n)\exp\{[(\Delta G^*_{in})_D - (\Delta G^*_{in})_H]/RT\} \qquad (1b)$$

In Eqn. (1a), $\Delta G^*_{in}(T)_D$ and $\Delta G^*_{in}(T)_H$ are the (temperature dependent) inner-shell intrinsic barriers[4] for the deuterated and protonated reactants, and $(\Delta G^*_{in})_D$ and $(\Delta G^*_{in})_H$ in Eqn. (1b) are the corresponding "classical" barriers; the former quantities include the effects of nuclear tunneling[4] which is expressed separately in Eqn. (1b) as a ratio of nuclear tunneling factors[4] (Γ_n^H/Γ_n^D). The terms $(\Delta G^*_{out})_D$ and $(\Delta G^*_{out})_H$ in Eqn. (1a) represent the outer-shell barriers in D_2O and H_2O solvent; in Eqn. (1b) the outer-shell contribution to the isotope effect is expressed instead as the preexponential ratio $(k^H/k^D)_{out}$. The remaining term in Eqn. (1), (ν_n^H/ν_n^D), is the corresponding ratio of the nuclear frequency factors ν_n. On the basis of a "preequilibrium" model of outer-sphere reactions, ν_n is related closely to the frequency of inner-shell vibrations.[4] The quantity (ν_n^H/ν_n^D) can therefore be taken as approximately equal to the ratio of the symmetric metal-oxygen frequencies[4] for OH_2 and OD_2, i.e. $(20/18)^{\frac{1}{2}} = 1.05$. The outer-shell contribution $(k^H/k^D)_{out}$ is estimated to be 1.06 from the dielectric continuum model, using the typical reactant radius of 3.5 Å and a reactant-electrode distance of 7 Å.[11] The inner-shell barriers were calculated from[4]

$$\Delta G^*_{in}(T) = \Delta G^*_{in}\left(\frac{4kT}{h\nu_{in}}\right) \tanh\left(\frac{h\nu_{in}}{4kT}\right) \qquad (2)$$

where ν_{in} is the effective (average) frequency of the inner-shell motion in the two oxidation states, the "classical" component ΔG^*_{in} being determined from

$$\Delta G^*_{in} = 0.5\ n\ \nu_{in}^2\ \pi^2 c^2 m\ \Delta a^2 \qquad (3)$$

where n is the number of bonds required to be stretched (or compressed), m is the ligand mass, and Δa is the difference in bond distances between the oxidized and reduced forms of the complex. Note that ΔG^*_{in} will be unaffected by ligand deuteration provided that the force constants remain the same (i.e. $m\nu_{in}^2$ = constant), as is normally observed.[14] The sole contribution to the isotope effect upon $\Delta G^*_{in}(T)$ is then contained in the nuclear tunneling ratio (Γ_n^H/Γ_n^D) [Eqn. (1b)]. [The presence of the factor 0.5 in Eqn. (3)

arises because only one reactant has to be activated for electrochemical exchange, rather than a pair of reactants as for the more commonly encountered[4] homogeneous self-exchange process.)

The values of $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ given in Table I were obtained by assuming that the only contribution to $\Delta G^{*}_{in}(T)$ arises from metal-oxygen ($M\text{-}OH_2$) vibrations. The average stretching frequency ν_{in} was taken as 430 cm^{-1} for $M\text{-}OH_2$;[4] Δa is known to be 0.14 Å for $Fe^{3+/2+}_{aq}$[15] and a 20Å for $Cr^{3+/2+}_{aq}$[16,17] which enabl $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ for these two couples to be found from Eqns. (1)-(3), given that $n=6$, and $\mu=18$ or 20 for $M\text{-}OH_2$ or $M\text{-}OD_2$ vibrations, respectively. Reliable values of Δa are as yet unavailable for the remaining redox couples $V^{3+/2+}_{aq}$ and $Eu^{3+/2+}_{aq}$. Nevertheless, the values of ΔG^{*}_{in} required for Eqn. (2) were obtained instead from the calculated value of ΔG^{*}_{in} for $Fe^{3+/2+}_{aq}$ (4.2 kcal mol^{-1}) by assuming that the variations in the observed values of k_{ex} between $Fe^{3+/2+}_{aq}$ and these two couples were due only to differences in ΔG^{*}_{in}.[18] The overall free energy barriers to electrochemical exchange, ΔG^{*}_{ex}, used for this purpose (Table I) were obtained from k_{ex} using $\Delta G^{*}_{ex} = -RT\ln(k_{ex}/Z_e)$, taking the frequency factor Z_e to be 5×10^{3} cm sec^{-1}.[18,19] In each case ν_{in} for $M\text{-}OH_2$ was taken as 430 cm^{-1}; variations in this quantity with the nature of the metal ion are only moderate[20] and unlikely to influence the result substantially.

Comparison of corresponding values of $(k^{H}_{ex}/k^{D}_{ex})_{ob}$ and $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ in Table I reveals that the observed values are substantially larger than the calculated quantities for $V^{3+/2+}_{aq}$, $Fe^{3+/2+}_{aq}$, and especially for $Cr^{3+/2+}_{aq}$, although the relatively small value of $(k^{H}_{ex}/k^{D}_{ex})_{ob}$ for $Eu^{3+/2+}_{aq}$ (1.1) is close to $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ (≈ 1.15). We have previously suggested that a major part of the observed isotope effects could be due instead to a larger outer-shell reorganization barrier in D_2O arising from ligand-solvent hydrogen bonding.[1]

These aquo redox couples are known to involve a substantial diminution in the extent of outer-shell solvent polarization in going from the oxidized to the reduced state,[2,21] so that significant cleavage of ligand-solvent hydrogen bonds are probably necessary in order to approach the transition state for reduction of the tripositive aquo cation. Such a component of the intrinsic reorganization energy is expected to be greater in D_2O as a result of the tendency of the deuterated solvent to form stronger and more extensive hydrogen bonds. Such an effect is not considered in current theoretical models which uniformly assume that the outer-shell solvent reorganization can be described in terms of a dielectric continuum.

An alternative explanation of the unexpectedly large values of $(k^{H}_{ex}/k^{D}_{ex})_{ob}$ is that they arise from nuclear tunneling associated with O-H ligand vibrational modes. Although these modes probably constitute only a minor component of the overall Franck-Condon barrier, their high frequencies (ca. 3,200-3,400 cm^{-1} [22]) can result in substantial contributions to the nuclear tunneling factor and hence to the observed isotope rate ratios[7,8] [Eqn. (2)]. This possibility was explored in the following manner. Estimates of the difference in the O-H bond distance, Δa_{O-H}, for the aquo ligands in the reduced and oxidized complexes were obtained by assuming that the differences betweeen corresponding values of $(k^{H}_{ex}/k^{D}_{ex})_{ob}$ and $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ are due entirely to inner-shell O-H vibrations. This entailed inserting trial values of Δa_{O-H} into Eqn. (3), assuming that $n=12$, $\nu_{in} = 3,200$ cm^{-1}, until agreement was reached between the observed isotope rate ratios and the values of $(k^{H}_{ex}/k^{D}_{ex})_{calc}$ arising from this component together with the other factors considered above. The resulting estimates of Δa_{O-H} are also listed in Table I. By and large, these values are somewhat greater than the usual variations in O-H bond distances (ca. 0.02-0.03 Å) determined by neutron diffraction for coordinated water, including that hydrogen bound to surrounding water, for a variety of crystalline hydrates containing multivalent metal cations.[23,24] Admittedly, the O-H bond in coordinated water will probably be significantly elongated upon increasing the charge of the central metal ion as a result of the combined effect of the larger polarizing charge and greater hydrogen bonding with surrounding water molecules oriented in the enhanced local field.[24] Nevertheless, in particular the estimated value of Δa_{O-H} for $Cr_{aq}^{3+/2+}$, 0.09 Å, seems unreasonably large.[25,26] These results suggest that other factors are at least partly responsible for the observed isotope effects, most likely from specific outer-shell reorganization as noted above.

Both these explanations for the observed isotope effects invoke the specific involvement of outer-shell solvent molecules. In this context it is interesting to note that the electrochemical isotope rate ratios for Cr_{aq}^{2+} and V_{aq}^{2+} oxidation are substantially (factors of 3-4 fold) larger than expected from the observed solvent isotope ratios for their homogeneous oxidation by $Co(NH_3)_6^{3+}$ on the basis of the usual Marcus electron-transfer model.[1] This model presumes that the inner- and outer-shell components of the overall free energy barrier arise from separable contributions due to each reactant that are the same (or similar) in the electrochemical and homogeneous environments. While this should be approximately correct for the inner-shell barrier since the metal-ligand vibrations are unlikely to be affected greatly by the surroundings, the reorganization energy of the nearby solvent is liable to be sensitive to the chemical and electrostatic environment in which the reactant undergoes activation.[28] The structure of the surrounding solvent is indeed expected to be markedly different for related electrochemical and homogeneous processes. Thus the latter reactions involve close approach of a pair of multicharged cations which is expected to disrupt the aquo ligand solvent hydrogen bonding in the region between the two reactants. The mercury surface should exhibit a milder perturbation upon the reactant solvation since the interfacial region contains only a small net charge density at the electrode potentials at which the electrochemical kinetics were monitored. Indeed there is evidence from studies of electrochemical double-layer effects that the secondary hydration sphere surrounding the aquo complexes remains at least partly intact in the transition state at the mercury-aqueous interface.[29,30] Consequently, the magnitude of the isotope effect arising from ligand-solvent hydrogen bonding is expected to be quite different in these homogeneous and heterogeneous environments. The relative magnitude of the effect is difficult to predict. However, the observed larger k^H/k^D ratios obtained in the latter environment are consistent with greater changes in the solvent polarization required to surmount the Frank-Condon barrier for electrochemical processes arising from the more extensive hydrogen bonding in the electrochemical compared with homogeneous transition states.

It is interesting to note that the magnitude of the observed isotope rate ratios $(k^H_{ex}/k^D_{ex})_{ob}$ are related closely to the size of the thermodynamic isotope effects as measured by the difference in the formal potentials, ΔE_f^{D-H}, for a redox couple in D_2O and H_2O solvents. Thus the substantially larger value of $(k^H_{ex}/k^D_{ex})_{ob}$ for $Cr^{3+/2+}_{aq}$ (2.8) compared with that for $Eu^{3+/2+}_{aq}$ (1.1) is mirrored by differences in ΔE_f^{D-H} of 57 and 9 mv, respectively[31] (Table I). These thermodynamic isotope effects appear to be due at least in part to an entropic destabilization of the tripositive oxidation state upon deuteration associated with ligand-solvent hydrogen bonding,[2] yielding greater differences in solvent polarization ("ordering") between the oxidized and reduced forms in D_2O. As noted above, such enhanced structural differences could also yield larger intrinsic barriers in D_2O resulting from the need to undergo greater changes in solvent polarization in order to form the nonequilibrium configuration appropriate for electron transfer.[1] The values of $(k^H_{ex}/k^D_{ex})_{obs}$ and ΔE_f^{D-H} for $Eu^{3+/2+}_{aq}$ are surprisingly small in comparison with those for the other aquo couples. A possible explanation is that $V_{aq}^{3+/2+}$, $Fe_{aq}^{3+/2+}$, and $Cr_{aq}^{3+/2+}$ involve electron transfer into 3d orbitals, yielding significant differences in the electron density of the aquo hydrogens,[32] and hence the extent of ligand-solvent hydrogen bonding (and the O-H bond length), between the two oxidation states. These differences should be smaller for the $Eu_{aq}^{3+/2+}$ couple since the electron is transferred into a 4f orbital which is shielded from the ligand orbitals.

Ammine Redox Couples

Redox couples containing ammine ligands are of particular interest in studies of isotope effects since, in contrast to aquo complexes, the ammine hydrogens can be deuterated independently of the surrounding solvent.[1] Substantial rate decreases were obtained for one-electron reduction of $Co(NH_3)_6^{3+}$, $Cr(NH_3)_6^{3+}$, and related complexes at a constant electrode potential E at the mercury-aqueous interface upon deuterating the ammine ligands. Thus, for $Co(NH_3)_6^{3+/2+}$ the observed isotope rate ratio $(k^{NH}/k^{ND})_{ob}^{E}$ equals 2.3 in aqueous solution.[1] Theoretical interpretation of these results is hampered by an absence of information on the formal potentials for these couples on account of the instability of the divalent ammines, so that the required values of k_{ex} are unknown. However, there is evidence that the difference in formal potentials, ΔE_f^{ND-NH}, for $Co(ND_3)_6^{3+/2+}$ versus $Co(NH_3)_6^{3+/2+}$ is small and positive (≈7 mv).[1] Although the formal potentials themselves are uncertain, accurate knowledge of E_f is unnecessary since the values of $(k^{NH}/k^{ND})_{ob}^{E}$ were found to be essentially independent of potential.[1] (Decreases in isotope ratios are predicted as the driving force is increased since the extent of nuclear tunneling will thereby be diminished.[7] However, this dependence should be scarcely detectable for the moderate range of overpotentials over which the electrochemical kinetics in ref. 1 were monitored.) Therefore the required value of the isotope rate ratio for electrochemical exchange of $Co(NH_3)_6^{3+/2+}$, $(k_{ex}^{NH}/k_{ex}^{ND})_{ob}$, can be estimated from the observed value of $(k^{NH}/k^{ND})_{ob}^{E}$ by correcting for the isotope effect upon the driving force using[1]

$$(k_{ex}^{NH}/k_{ex}^{ND})_{ob} = (k^{NH}/k^{ND})_{ob}^{E} + \exp(\alpha F \Delta E_f^{ND-NH}/RT) \quad (4)$$

where α is the electrochemical transfer coefficient for $Co(NH_3)_6^{3+}$ reduction. Inserting the above values of $(k^{NH}/k^{ND})_{ob}^{E}$ and ΔE_f^{ND-NH} into Eqn. (4) and assuming that $\alpha = 0.5$ yields the estimate $(k_{ex}^{NH}/k_{ex}^{ND})_{ob} \approx 2.5$.

The corresponding theoretical prediction using Eqns. (1)-(3) is obtained from: $(\nu_n^H/\nu_n^D) = (20/17)^{\frac{1}{2}} = 1.08$, $\Delta a = 0.22$ Å,[33] $\nu_{in} = 409$ cm^{-1};[36] yielding $(k_{ex}^{NH}/k_{ex}^{ND})_{calc} = 1.18$. [No outer-shell contribution is included in this estimate since the solvent was not deuterated.] Again, this calculated isotope ratio is much smaller than the experimental value of 2.5.

We have noted previously that the corresponding isotope ratio $(k^{NH}/k^{ND})_{ob}^{hom}$ for the homogeneous reduction of $Co(NH_3)_6^{3+}$ by $Cr(bpy)_3^{2+}$ in aqueous solution (where bpy = 2,2'-bipyridine) is markedly smaller (1.35) than $(k^{NH}/k^{ND})_{ob}^{E}$ for $Co(NH_3)_6^{3+}$ electroreduction (2.3) even though the Marcus model predicts equal isotope ratios under these conditions.[1] This discrepancy seems likely to be due to the same causes as those discussed above in connection with the observed similar behavior of the aquo couples. The observation that $(k_{ex}^{NH}/k_{ex}^{ND})_{ob} > (k_{ex}^{NH}/k_{ex}^{ND})_{calc}$ for electrochemical exchange may therefore be again due to the effects of specific ligand-solvent hydrogen bonding,[1] although the extent of such interactions appears to be smaller than for otherwise similar aquo couples.[21] Unfortunately, there appears to be no direct information on the effect of complexation and hydrogen bonding on N-H bond distances. The N-H bonds are presumably lengthened slightly in going from $Co(NH_3)_6^{2+}$ to $Co(NH_3)_6^{3+}$ in view of the minor (ca 100 cm^{-1}) decrease in the N-H stretching frequencies.[37] However, there appears to be little influence on these bonds from hydrogen bonding with the surrounding solvent on the basis of the very similar N-H stretching frequencies observed in crystalline solids and in aqueous solution.[38]

Buhks et al have recently calculated an isotope ratio of 1.26 for the effect of ligand deuteration upon $Co(NH_3)_6^{3+/2+}$ homogeneous self exchange at 25°C using a similar approach based on a quantum mechanical model.[7] This result corresponds to a value of approximately $(1.26)^{\frac{1}{2}} = 1.12$ for either electrochemical exchange or homogeneous "exchange" of $Co(NH_3)_6^{3+/2+}$ with an inert coreactant.[7,39] (The square root arises from the involvement of only one $Co(NH_3)_6^{3+/2+}$ couple in the exchange reactions rather than a pair of reactants as in homogeneous self exchange.[9]) The difference between this value of $(k_{ex}^{NH}/k_{ex}^{ND})_{calc}$ and that noted above (1.18) arises chiefly from the larger value of Δa for $Co(NH_3)_6^{3+/2+}$ used here.[33] Buhks et al noted that their predicted value of $(k_{ex}^{NH}/k_{ex}^{ND})_{calc}$ is significantly smaller than the experimental value (1.36) for $Co(NH_3)_6^{3+}$ reduction by $Cr(bpy)_3^{2+}$, and also suggested that the discrepancy may be due to an additional contribution to the latter from high frequency N-H modes.[7] Similarly to the electrochemical isotope ratio for $Co(NH_3)_6^{3+}$ reduction $(k^{NH}/k^{ND})^{E}_{ob}$ that is discussed above, this experimental value for homogeneous reduction using a fixed reductant will differ from that for true homogeneous "exchange" of $Co(NH_3)_6^{3+/2+}$ on account of the change in the driving force upon deuteration of the ammine ligands. Assuming that ΔE_f^{D-H} for $Co(NH_3)_6^{3+/2+}$ equals 7 mv, using Eqn. (4)[39] a value of $(k_{ex}^{NH}/k_{ex}^{ND})_{ob}$ equal to 1.55 is obtained for $Co(NH_3)_6^{3+/2+}$ "exchange" with $Cr(bpy)_3^{3+/2+}$, again noticeably larger than the calculated values.

Acknowledgments

We are grateful to Ephraim Buhks, George McLendon and Henry Taube for communicating some results (refs. 8 and 34) prior to publication. This work is supported in part by the Office of Naval Research and the Air Force Office of Scientific Research.

References and Notes

(1) M. J. Weaver, P. D. Tyma, S. M. Nettles, J. Electroanal. Chem. 114, 53 (1980).

(2) M. J. Weaver, S. M. Nettles, Inorg. Chem. 19, 1641 (1980).

(3) R. A. Marcus, J. Chem. Phys. 44, 679 (1965).

(4) B. S. Brunschwig, J. Logan, M. D. Newton, N. Sutin, J. Am. Chem. Soc. 102, 5798 (1980).

(5) P. Siders, R. A. Marcus, J. Am. Chem. Soc. 103, 741 (1981).

(6) E. Buhks, M. Bixon, J. Jortner, G. Navon, J. Phys. Chem. 85, 3759 (1981).

(7) E. Buhks, M. Bixon, J. Jortner, J. Phys. Chem. 85, 3763 (1981).

(8) T. Guarr, E. Buhks, G. McLendon, submitted for publication.

(9) Although the contemporary treatments of outer-sphere electron transfer described in refs. 3-7 have been applied almost exclusively to homogeneous reactions, they are also applicable with minor modification to electrochemical processes.[10] In particular, the relations derived for homogeneous self-exchange reactions can be transposed directly to describe the corresponding electrochemical "exchange" reactions, i.e. the kinetics determined at the formal potential for the redox couple under consideration. Relations such as Eq (1) will apply to nonadiabatic as well as adiabatic processes on the basis of a semiclassical model,[4] provided that the transmission coefficient for electron tunneling is equal in the protonated and deuterated systems. Minor differences in the contributions of the preexponential factor to the isotope ratio between adiabatic and nonadiabatic pathways arise when using the model described in ref. 6.

(10) M. J. Weaver, in "Inorganic Reactions and Methods", J. J. Zuckerman (ed.), Verlag Chemie (pub.) in press.

(11) In ref. 7, the outer-shell solvent contribution to the isotope ratio k^H/k^D for homogeneous self exchange was calculated to be ≈ 0.90 using the dielectric continuum model. This result appears to be in error, being apparently based on an inappropriate value for the refractive index n_i for liquid D_2O. The original literature values for n_i for D_2O are slightly higher than those for H_2O over a range of temperatures at the same wavelength of light.[12] Thus at 25°C, $n_i = 1.3329$ (H_2O) and 1.3288 (D_2O) using the Na-D line.[12] Combining these with the corresponding static dielectric constants $D = 78.3$ (H_2O) and 77.95 (D_2O) at 25°C,[13] yields values for the quantity $\beta (= n_i^{-2} - D^{-1})$[7] of 0.5500 ($H_2O$) and 0.5535 ($D_2O$), which using the usual dielectric continuum expression[3] leads to $k^H/k^D \approx 1.08$. A somewhat smaller value of k^H/k^D (1.06) is obtained for electrochemical exchange[1] because only one reactant is activated, rather than a pair of reactants for homogeneous self exchange.

(12) D. Eisenberg, W. Kauzman, "The Structure and Properties of Water", Oxford University Press, Oxford, 1969, p. 198; E. Reisler, H. Eisenberg, J. Chem. Phys. 43, 3875 (1965); H. Eisenberg, J. Chem. Phys. 43, 3887 (1965).

(13) G. Nemethy, H. A. Scheraga, J. Chem. Phys. 41, 680 (1964).

(14) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd, ed., Wiley, N. Y., 1978.

(15) N. J. Hair, J. K. Beattie, Inorg. Chem. 16, 245 (1977).

(16) B. S. Brunschwig, C. Creutz, D. H. McCartney, T-K. Sham, N. Sutin, Disc. Far. Soc. 74 (1982) in press.

(17) The estimate $\Delta a = 0.20$ Å for $Cr_{aq}^{3+/2+}$ obtained from EXAFS data is an average value taken over all six $Cr-OH_2$ bonds.[16] Since Cr_{aq}^{2+} exhibits a noticeable Jahn Teller distortion from octahedral symmetry, a pair of $Cr-OH_2$ bonds have a markedly larger value of Δa (and probably a slightly smaller value of ν_{in}) than the remaining four bonds.[16] Nevertheless, the use of the single value $\Delta a = 0.20$ Å is adequate for the present purposes since only the overall value of ΔG^*_{in} appears in Eq (2) rather than the individual values of n and Δa.

(18) Strictly speaking, the differences in k_{ex} between the various redox couples may be due to variations in $\Delta G^*_{in}(T)$, ΔG^*_{out}, and also in the electronic transmission coefficient κ_{el}. However, the predominant variable is likely to be ΔG^*_{in}.

(19) M. J. Weaver, J. Phys. Chem. 84, 568 (1980).

(20) I. Nakagawa, T. Shimanouchi, Spectrochim. Acta 20, 429 (1964).

(21) E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, M. J. Weaver, J. Am. Chem. Soc. 101, 1131 (1979).

(22) I. Gamo, Bull. Chem. Soc. Japan 34, 760, 765 (1961).

(23) (a) W. C. Hamilton, J. A. Ibers, "Hydrogen Bonding in Solids", Benjamin New York, N. Y., 1968, p. 212; (b) M. Falk, O. Knop, in "Water: A Comprehensive Treatise," F. Franks (ed), Vol. 2, Plenum Press, New York, N. Y., 1973, Chapter 2.

(24) Although the O-H bond distances for coordinated water in the large numbers of crystalline hydrates for which neutral diffraction data are available vary over the range ca. 0.95 to 1.03 Å, these values refer to water molecules in a variety of electrostatic and stereochemical environments.[23] The bond distances of greatest relevance to $M_{aq}^{3+/2+}$ redox couples clearly will involve coordinated water that is also hydrogen bonded to surrounding water molecules. From the average O...O bond distances noted for various divalent and trivalent cations, 2.82 and 2.68 Å, respectively,[23b] combined with the correlation seen between the O-H and O...O bond distances [Figure 10 of ref 23 b], it is deduced that the O-H bond length will typically increase by ca. 0.02 Å from the dipositive to tripositive oxidation state.

(25) The result $\Delta a = 0.09$ Å for $Cr_{aq}^{3+/2+}$ represents an "average" value since it was obtained assuming n=12. If the predominant changes in the O-H bond distance occur for a pair of *trans* ligands, then n effectively equals 2, yielding $\Delta a = 0.15$ Å.

(26) If indeed such large values of Δa occur for these redox couples, then one would expect the O-H stretching frequencies in the higher oxidation state to be noticeably smaller than the "typical" values in the range ca. 3200-3400 cm^{-1}.[23b,27] This would thereby decrease the effective frequency ν_{in} in Eq (3), yielding even larger estimates of Δa from this relation.

(27) See for example, M. D. Newton, J. Chem. Phys. 67, 5535 (1977).

(28) M. J. Weaver, E. L. Yee, Inorg. Chem. 19, 1936 (1980).

(29) M. J. Weaver, T. L. Satterberg, J. Phys. Chem. 81, 1772 (1977).

(30) M. J. Weaver, H. Y. Liu, Y. Kim, Can. J. Chem. 59, 1944 (1981).

(31) Such differences in thermodynamic driving force for a given electrochemical reaction in D_2O and H_2O are themselves taken into account by evaluating the rate constants at the appropriate formal potential in each solvent.

(32) This effect has indeed been obtained from a theoretical study of inner-shell bonding in the $Fe_{aq}^{3+/2+}$ couple: J. A. Jafri, J. Logan, M. D. Newton, Israel J. Chem. 19, 340 (1980).

(33) The value $\Delta a = 0.22$ Å has recently been obtained from EXAFS measurements; a similar value (0.21 Å) has also been obtained from EXAFS and x-ray crystallography for the closely related $Co(en)_3^{3+/2+}$ couple.[16,34] This estimate for Δa is considered to be more reliable than the earlier value of Δa for $Co(NH_3)_6^{3+/2+}$ of 0.18 Å.[35]

(34) D. A. Geselowitz, P. R. Jones, H. Taube, unpublished results.

(35) H. C. Stynes, J. A. Ibers, Inorg. Chem. 10, 2304 (1971).

(36) Average stretching frequency for $Co(NH_3)_6^{3+/2+}$; from data given in T. Shimanouchi, T. Nakayawa, Spectrochim. Acta 18, 80 (1962).

(37) K. H. Schmidt, A. Muller, Coord. Chem. Res. 19, 41 (1976).

(38) T. W. Swaddle, P. J. Craig, P. M. Boorman, Spectrochim. Acta 26A, 1559 (1970).

(39) The electrochemical isotope rate ratio $(k^{NH}/k^{ND})_{ob}^{E}$, i.e. that determined at a constant electrode potential, is analogous to the use of a fixed reducing agent, such as $Cr(bpy)_3^{2+}$ in the present case.

Table I. Comparison between Observed and Calculated Deuterium Isotope Effects for Electrochemical Exchange of Some Aquo Couples at 25°C

Redox Couple[a]	k_{ex}[b] cm sec^{-1}	ΔG^*_{ex}[c] kcal mol^{-1}	$(k^H_{ex}/k^D_{ex})_{ob}$[d]	$(k^H_{ex}/k^D_{ex})_{calc}$[e]	ΔE_f^{D-H}[f] mv	Δa_{O-H}[g] Å
$V^{3+/2+}_{aq}$	$1x10^{-3}$	9.1	1.5	1.16	53	0.05
$Fe^{3+/2+}_{aq}$	$\sim 1x10^{-4}$	$\sim$10.5	1.5	1.18	43	0.05
$Eu^{3+/2+}_{aq}$	$8x10^{-5}$	10.6	1.1	$\approx$1.15	9	0
$Cr^{3+/2+}_{aq}$	$2x10^{-6}$	12.8	2.8	1.22	57	0.09

[a] "aq" represents either OH_2 or OD_2 ligands

[b] Work-corrected rate constant for electrochemical exchange of given redox couple at mercury-aqueous interface; from ref. 1.

[c] Free energy of activation for electrochemical exchange, determined from k_{ex} using ΔG^*_{ex} = $RT\ln(k_{ex}/Z_e)$, where Z_e is taken as 5 x 10^3 cm sec^{-1}.

[d] Ratio of observed value of k_{ex} determined in H_2O to that in D_2O; from ref. 1.

[e] Calculated value of k^H_{ex}/k^D_{ex} obtained using Eqns. (1)-(3) assuming that inner-shell component arises from metal-oxygen vibrations (see text).

[f] Difference in formal potential in D_2O to that in H_2O at ionic strengths 0.1-0.2, measured versus an aqueous s.c.e.; from ref. 2.

[g] Estimated difference in average O-H bond distance for aquo ligand between oxidized and reduced forms of redox couple; obtained as outlined in text.

END

DATE
FILMED

5 - 83

DTIC