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Deuterium Isotope Effects on Outer-Sphere Electron-Transfer Reactions

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In this paper we present a theoretical study of the kinetic isotope effect (KIE) on outer-sphere electron-transfer (ET) reactions, which provides one of the manifestations of quantum effects in such systems. The KIE arising from the deuteration of the ligands in the first coordination layer originates from frequency changes and from distortion of the equilibrium configurations of the totally symmetric stretching modes for the motion of the ligands in the two oxidation states. On the basis of model calculations, we assert that the dominating contribution to the KIE originates from the changes in the ion–ligand equilibrium configurations accompanying the ET process. The KIE, which is expressed in terms of the ratio of the rate constants, k_H/k_D, is found to be normal and small at room temperature, being $k_H/k_D = 1.26$ for the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ exchange and $k_H/k_D = 1.12$ for the $Co(NH_3)_6^{3+}$–$Cr(bpy)_3^{2+}$ exchange, both calculated at 25 °C. The calculated KIE $k_H/k_D = 1.12$ for the $Co(NH_3)_6^{3+}$–$Cr(bpy)_3^{2+}$ exchange at 25 °C is significantly lower than the experimental value of $k_H/k_D = 1.36$. We have examined the dependence of the KIE on the energy gap, demonstrating that k_H/k_D exhibits a maximum for symmetric ET reactions. A dramatic temperature dependence of k_H/k_D is predicted with k_H/k_D exhibiting a very large temperature-independent value at low temperatures, decreasing with increasing temperature, while the isotope effect is completely eroded in the high-temperature classical limit.

I. Introduction

Quantum effects on outer-sphere electron-transfer (ET) reactions in solution provide a manifestation of nuclear tunneling phenomena.[1-7] The characteristic frequencies associated with metal–ligand motion in complex cations are[2,8] in the range $\hbar\omega_c = 250$–500 cm^{-1}, slightly exceeding the thermal energy k_BT at room temperature, i.e., $h\omega_c \simeq k_BT$–$2k_BT$. For ET reactions associated with a substantial inner-sphere reorganization energy, the quantum effects on the absolute rate of reaction are quite modest,[9] resulting in the enhancement of the rate at room temperature by ~1 order of magnitude. Another quantum effect on ET reactions involves the deuterium isotope effect on the ET rates, which is the subject matter of the present paper.

The experimental information currently available concerning deuterium isotope effects on the rates of ET reactions is rather scarce. Some of the available kinetic data exhibit a large isotope effect, e.g., the rate of the Fe^{2+}–Fe^{3+} exchange reaction is lowered by a numerical factor of ~2 in D_2O relative to H_2O.[10] In the reactions of $Co(NH_3)_5H_2O^{3+}$ with $Cr(bpy)_3^{2+}$ and with $Cr(H_2O)_6^{2+}$, considerable deuterium isotope effects upon deuteration of the H_2O molecules in the coordination layer were discovered,[11] with the ET rates decreasing by numerical factors 2.6 and 3.8, respectively. These large deuterium isotope effects were interpreted in terms of a mechanism involving inner-sphere H-atom transfer.[10,11] There exists some pertinent information concerning ET processes which can unambiguously be attributed to outer-sphere ET reactions. One such case is the oxidation of $Cr(bpy)_3^{2+}$ by $Co(NH_3)_6^{3+}$.[6] For this reaction no solvent deuterium isotope effect was found.[11] On the other hand, a decrease of the ET rate by a factor of 1.36 was found[11] upon deuteration of the ammonia molecules in the first coordination layer. More recently, the kinetic isotope effect on the reduction of various cobalt(III) pentaammine complexes by Cr(II) and by V(II) was investigated.[12] At least for several of these complexes, such as the pyridine complex, the ET process presumably involves outer-sphere ET. In such cases a kinetic deuterium isotope effect up to 1.5 was reported.[12]

In this paper we present a theoretical study of the kinetic deuterium isotope effect on outer-sphere ET reactions, utilizing the quantum-mechanical formalism of the preceding paper.[9] In the next section, we discuss the solvent isotope effect, originating from changes in the dielectric properties of the exterior solvent upon deuteration. In section III we discuss the main cause of the isotope effect originating from the changes in the metal–ligand vibrational frequencies, which are induced by the deuteration of the ligands in the first coordination layer. We demonstrate that the molecular property, which is responsible for the isotope effect, is the distortion of the high-frequency modes upon changing the oxidation state. We shall be able to provide some predictions concerning the effects of the energy gap and of the temperature on the isotope effect in outer-sphere ET.

II. Solvent Isotope Effect

We consider first the influence of the deuteration of the exterior solvent on the deuterium isotope effect on outer-sphere ET. Our basic assumptions are that the first coordination layer is invariant and that there are no specific interactions between the exterior solvent and the first coordination layer of the complex ion. Accordingly, the solvent effect simply originates from changes in the dielectric properties of the solvent. The dielectric behavior influences the ET processes by changing the Marcus solvent reorganizaton energy, E_s, which is proportional to $\beta = n^{-2} - D^{-1}$, where n is the refraction index and D is the

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TABLE I: Diagonal Elements of G-Matrix, Skeletal Vibrational Frequencies for $Co(ND_3)_6^{2+,3+}$ and $Co(NH_2)_6^{2+,3+}$

$G_{\alpha\alpha}{}^{a}$	ω_α, cm^{-1}	$Co(ND_2)_6^{2+}$	$Co(ND_3)_6^{3+}$	$Co(NH_3)_6^{2+}$	$Co(NH_3)_6^{3+}$
μ	$\omega_1(A_{1g})$	329	455	357	494
μ	$\omega_2(E_g)$	235	407	255	442
$\mu + 2\mu_0$	$\omega_3(F_{1u})$	294	429	325	475
$2(\mu + 4\mu_0)$	$\omega_4(F_{1u})$	179	308	192	331
4μ	$\omega_5(F_{2g})$	172	297	187	322
2μ	$\omega_6(F_{2u})$	132	227	143	246

[a] Reference 14. μ and μ_0 are reciprocal of masses of a ligand and of a metal center, respectively.

dielectric constant. The quantity β (at 25 °C) varies from 0.550 for H_2O to 0.546 in D_2O, thus being responsible for a decrease of ~1% in the solvent reorganization energy of heavy water. The ET transition probability for a symmetrical reaction is proportional to $\exp\{-E_s/4k_BT\}$. When one takes, for example, the case of the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ exchange (E_s = 28 kcal mol^{-1}),[8] the resulting solvent isotope effect induced by deuteration of the exterior solvent is $k_H/k_D \simeq 0.90$. We note in passing that this small effect corresponds to an inverse isotope effect. The inverse solvent isotope effect is expected to increase toward unity with increasing the electronic energy gap $|\Delta E|$ of the reactants. The ratio k_H/k_D assumes the value of unity for activationless reactions ($\Delta E = -E_s$) and for barrierless reactions ($\Delta E = E_s$).

Applying these considerations to the ET reaction between $Co(NH_3)_6^{3+}$ and $Cr(bpy)_3^{2+}$, estimating $E_s \approx 1$ eV, and taking ΔE = −0.57 eV (the redox potential),[13] one obtains a solvent kinetic isotope effect of k_H/k_D = ~0.94. This value has to be compared with the experimental value[11] of about unity for the same reaction.

III. Role of Intramolecular Modes on Kinetic Isotope Effects

We now proceed to examine the effect of deuterium isotope substitution in the first coordination layer on the ET rate. Our evaluation of the kinetic isotope effect is based on the assumption that, upon the deuteration of the ligands, there is no change in the electronic properties of the complex. Therefore, one remains with the same energy surface, whereupon the equilibrium configurations and force constants remain unchanged. Furthermore, we assume that there are no contributions to the isotope effect from the internal modes of the ligands. The assumption that the values of force constants are invariant is expressed formally as follows:

$$G_{H\kappa\kappa}{}^{-1}\omega_{H\kappa}{}^2 = G_{D\kappa\kappa}{}^{-1}\omega_{D\kappa}{}^2 \qquad \kappa = 1, ..., n \tag{1}$$

where $\omega_{H\kappa}$ and $\omega_{D\kappa}$ are the frequencies of the metal-protonated ligand and the metal-deuterated ligand, respectively. $G_{H\kappa\kappa}$ and $G_{D\kappa\kappa}$ are the elements of the **G** matrix for the metal–ligand modes, involving the protonated and the deuterated ligands, respectively. The diagonal elements of the reciprocal-mass **G** matrix for an octahedral complex ion[14] are given in Table I. The relation between totally symmetric frequencies of the protonated and deuterated complex ions is given by

$$m_H\omega_H{}^2 = m_D\omega_D{}^2 \tag{1a}$$

where m_H and m_D are masses of protonated and deuterated ligands, respectively. Here and in what follows we shall omit the mode index κ. Making use of the frequencies of the $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ complexes, together with eq 1a, we have calculated the skeletal vibrational frequencies for the $Co(ND_3)_6^{2+}$ and $Co(ND_3)_6^{3+}$ complexes which are summarized in Table I.

Utilizing this set of metal–ligand frequencies (Table I), together with the information[8,9] concerning the changes in the bond lengths, which are assumed to be invariant to deuteration of the ligands, one can perform detailed quantum-mechanical calculations of the isotope effect on the ET rates. Making use of eq 15 of the preceding paper,[9] one obtains the ratio between the Franck–Condon factors for the $Co(NH_3)_6^{2+,3+}$ and $Co(ND_3)_6^{2+,3+}$ exchange reactions to be 1.26 at 25 °C. This isotope effect results from two contributions: (a) a numerical factor of 1.02 from the ratio of the preexponential factors in eq 16 of ref 9, which originate from the change of the frequencies of 15 modes in each ion, and (b) a numerical factor of 1.22 from the ratio of the exponentials in eq 16 of ref 9, which arise from the stretching mode of each complex ion.

We conclude that the effect of frequency changes on the isotope effect is minor and that the major contribution to the kinetic deuterium kinetic effect arises from the difference in the contributions of the totally symmetric vibrational modes to the Franck–Condon factors. This dominating contribution can be expressed in the form

$$k_H/k_D = \exp(Y_D - Y_H) \tag{2}$$

We shall follow the notation of the previous paper,[9] taking

$$Y = 2(\Delta d)^2\omega'\omega''[\omega' \coth \nu'' + \omega'' \coth \nu']^{-1} \tag{3}$$

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

and Δd is the reduced displacement

$$(\Delta d)^2 = 6(\Delta r)^2m/\hbar \tag{4}$$

where distinct oxidation states are distinguished by one prime and two primes, respectively. Finally, the subscripts H and D in eq 2 label the quantities corresponding to the "normal" ion and to the deuterated ion, respectively. Evidently, the isotope effect is temperature dependent. For the $Co(NH_3)_6^{2+,3+}$ exchange k_H/k_D varies from 1.12 at 70 °C to 1.26 at 25 °C.

Equation 2 provides a reasonable description of the effects of intramolecular modes on the kinetic isotope effect. The limiting cases of this isotope effect are of interest. At high temperatures $\nu \ll 1$, so that eq 2 yields $k_H/k_D = 1$, whereupon all of the quantum effects disappear. As is well-known, in this classical limit the intramolecular reorganization energy is proportional to the force constant and does not change on isotopic ligand substitution. The effect of deuteration on the rates originates from the role of intramolecular metal–ligand modes and corresponds to a pure quantum-mechanical effect.

In the low-temperature approximation, $\nu \gg 1$. Equation 2 then predicts the greatest isotope effect, being equal to

$$k_H/k_D = \exp\{Y_H(T \rightarrow 0)[(m_D/m_H)^{1/2} - 1]\} \tag{5}$$

where

$$Y(T \rightarrow 0) = 2(\Delta d)^2\omega'\omega''/(\omega' + \omega'') \tag{6}$$

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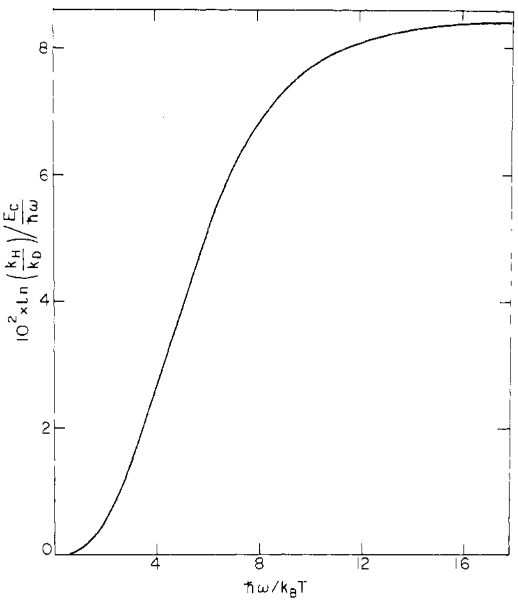

Figure 1. Temperature dependence of deuterium kinetic isotope effect for symmetric electron-exchange reactions ($\Delta E = 0$) between hexaammine complexes.

For $Co(NH_3)_6^{2+,3+}$ electron-exchange reaction, eq 5 predicts a considerable deuterium isotope effect of ~30 at low temperatures.

In order to obtain an overview of the temperature dependence of k_H/k_D for the symmetric ET process ($\Delta E = 0$), one can use a simplified single stretching mode with unchanged average frequency of[9]

$$\omega = 2\omega'\omega''/(\omega' + \omega'') \tag{7}$$

Then the use of eq 28 of ref 9 yields the following expression for the kinetic isotope effect:

$$k_H/k_D = \exp[-(E_c/\hbar\omega_H) \tanh \nu_H + (E_c/\hbar\omega_D) \tanh \nu_D] = \exp\left\{\frac{E_c}{\hbar\omega_H}[\{m_D/m_H\}^{1/2} \tanh (\nu_H\{m_H/m_D\}^{1/2}) - \tanh \nu_H]\right\}$$

$$\nu_H = \hbar\omega_H/4k_BT \qquad \nu_D = \hbar\omega_D/4k_BT \tag{8}$$

where E_c is the reorganization energy of the intramolecular vibrational modes which are affected by deuteration of the ligands. E_c is given by $E_c = (\Delta d)^2(\hbar\omega)^2$, where $(\Delta d)^2$ is given by eq 4, while the frequency corresponds either to ω_H or to ω_D. It is apparent that E_c is invariant with respect to isotopic substitution. Figure 1 portrays the temperature dependence of the isotope effect which is expressed in terms of the reduced quantity $\ln (k_H/k_D)/(E_c/\hbar\omega)$. These results clearly demonstrate that the kinetic isotope effect reaches its highest low-temperature value as $\hbar\omega/k_BT \geq 10$. For characteristic frequencies of 400 cm^{-1}, the saturation of the low-temperature isotope effect occurs at a temperature of $T \leq 60$ K. In the high-temperature range at room temperature and at higher temperatures, where $\nu \leq 0.5$, one can utilize a series expansion for tanh ν which appears in eq 8, whereupon eq 8 predicts that

$$k_H/k_D = \exp[(E_c/3\hbar\omega_H)\nu_H^3(1 - m_H/m_D)] \tag{9}$$

Thus, the isotope effect is expected to rise fast with decreasing temperature, being proportional to $\exp(\nu^3)$, i.e., $\exp(\alpha T^{-3})$, where α is a numerical factor.

Another point to consider is the effect of the electronic energy gap, ΔE, between the reactants on the ratio k_H/k_D. We shall treat a model where the frequencies of ET donor and acceptor for each isotopic composition are identical. As we already know, the effect of frequency differences between the two oxidation states on the rate constant is small. When the frequency changes are disregarded, the Franck–Condon factors can be expressed in the form $\exp(F)$, where the function F can be well represented in terms of the saddle-point approximation[2,8,9]

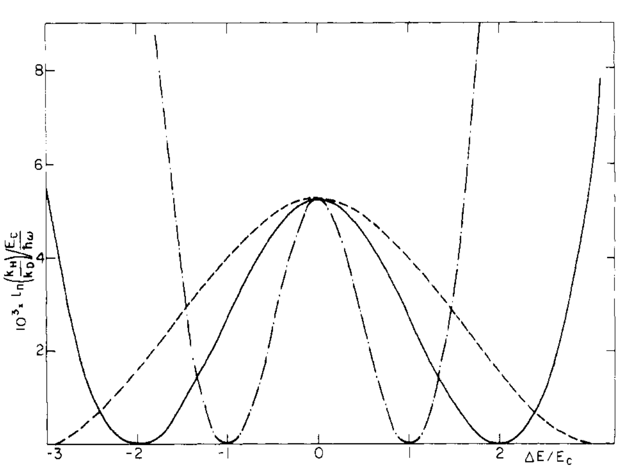

Figure 2. Deuterium isotope effect for ET between ammine complexes as a function of the reduced electronic energy gap $\Delta E/E_c$. E_r is the total reorganization energy $E_r = E_s + E_c$. The parameters are as follows: $\hbar\omega_H/k_BT = 2.0$ and $E_s/E_c = 0$ (–·–), $E_s/E_c = 1$ (—), $E_s/E_c = 2$ (– – –).

$$F = -\frac{E_s}{4k_BT}(1 - y^2) - \frac{\Delta E}{2k_BT}(y + 1) - \frac{E_c}{\hbar\omega}\left[\coth 2\nu - \frac{\cosh 2\nu y}{\sinh 2\nu}\right] \tag{10}$$

The saddle point y is determined by the relation

$$\Delta E = E_s y + E_c\left(\frac{\sinh 2\nu y}{\sinh 2\nu}\right) \tag{11}$$

The kinetic isotope effect, originating from isotope ligand substitution, can be evaluated by the following expression:

$$k_H/k_D = \exp[F(\Delta E,E_s,E_c,T,\omega_D,y_D) - F(\Delta E,E_s,E_c,T,\omega_H,y_H)] \tag{12}$$

This relation is plotted in Figure 2 for various ratios of the solvent reorganization energy E_s to the reorganization energy E_c of the quantum modes. The results demonstrate the following: (1) The maximum value of the isotope effect is achieved for symmetric reactions ($\Delta E = 0$, $y = 0$). (2) The isotope effect decreases with increasing value of $|\Delta E|$ and reaches its minimum value, close to unity, in the case of activationless and barrierless reactions, i.e., $\Delta E = -(E_s + E_c)$, $y = -1$, and $\Delta E = E_s + E_c$, $y = 1$, respectively. (3) For highly exothermic or very endothermic reactions $|\Delta E| > E_s + E_c$, $|y| > 1$, the kinetic isotope effect increases with increasing the energy gap $|\Delta E|$. (4) ln (k_H/k_D) vs. $\Delta E/E_c$ exhibits a bell-shaped curve whose width depends on the value of the solvent reorganization energy being equal to $2(E_s/E_c + 1)$. Therefore, for the ET reactions in the "normal region", which are usually characterized by a large solvent reorganization energy, $E_s \geq 1$ eV and $E_s/E_c \gtrsim 1$, an estimate of k_H/k_D can be approximated by its value for the symmetric reactions, given by the analytic expressions 8 and 9.

Our model calculations of the deuterium kinetic isotope effect on outer-sphere ET demonstrate that the dominating contribution to the ratio k_H/k_D originates from the change in the metal–ligand equilibrium configuration accompanying the ET process. Our treatment assumed that the force constants are invariant with respect to the isotopic substitutions of the ligands, while the ligand–ion frequencies (eq 1a) and the reduced displacements (eq 4) are affected by it. The present formalism results in a normal isotope effect, i.e., $k_H/k_D \geq 1$. We shall now confront the theory with the available experimental data. Making use of eq 10–12, together with the available data for the $Co(NH_3)_6^{3+}$ ion (Table I), we obtain $k_H/k_D = 1.12$ for the kinetic isotope effect originating from the deuteration of the ammonia molecules, on electron exchange between $Co(NH_3)_6^{3+}$ and $Co(bpy)_3^{2+}$ at 25 °C. This isotope effect is due to the deuteration of the coordination layer, which is characterized by a large intramolecular reorganization energy of ~1 eV. This predicted isotope effect is lower than the experimental value of 1.36 reported[11] for this reaction, and the values of up to 1.5 reported[12] for outer-sphere ET reactions of cobalt pentaammine complexes.

IV. Concluding Remarks

We have demonstrated that deuteration of the ligands in the first coordination layer is expected to give rise to a normal, small, isotope effect at room temperature. From the practical point of view, we only managed to predict the general trend and magnitude of the isotope effect but did not succeed in obtaining a quantitative fit for the numerical value of k_H/k_D for the $Co(NH_3)_6^{3+}$–$Cr(bpy)_3^{2+}$ ET reaction at 25 °C. A possible source of the discrepancy between the theoretical value $k_H/k_D = 1.12$ and the experimental value $k_H/k_D = 1.36$ may arise from an additional contribution, due to small changes in the N–H and N–D intramolecular bond lengths of the NH_3 (or ND_3) molecules in the first coordination layer, which are induced by the change in the charge of the cation. Our current ignorance of the magnitude of this change in the intramolecular bond lengths precludes the estimate of its effect on the ET rate. From the point of view of general methodology, we were able to demonstrate the quantum effects of nuclear tunneling on ET reactions. The modest magnitude of the kinetic isotope effect at room temperature, emerging from the present calculations, indicates that quantum effects on room-temperature outer-sphere reactions are not very dramatic, this conclusion being in accord with the analysis of quantum effects on the absolute rates of ET reactions.[9]

The present work provides some new theoretical predictions concerning the energy-gap dependence and the temperature dependence of the kinetic isotope effect of ET. Regarding the dependence of k_H/k_D on the energy gap, we find the following: (1) k_H/k_D exhibits a maximum for symmetric reactions ($\Delta E = 0$). (2) k_H/k_D decreases with increasing $|\Delta E|$ in the "normal" region. (3) The ΔE dependence of $\ln (k_H/k_D)$ in the normal region is expected to be described by a bell-shaped curve peaking at $\Delta E = 0$. A similar dependence of the isotope effect on ΔE is exhibited for proton transfer reactions.[15–17] With regard to the temperature dependence of k_H/k_D, we predict the following: (a) $\ln (k_H/k_D)$ attains a constant large value at low temperatures ($k_BT \ll \hbar\omega$) which, according to the data of Figure 1, is roughly of the form

$$k_H/k_D = \exp(0.09E_c/\hbar\omega) \qquad (T \to 0)$$

for symmetric ET reactions. (b) At higher temperatures k_H/k_D decreases with increasing temperature. (c) In the temperature range 0–70 °C, eq 9 predicts that $\ln (k_H/k_D)$ is expected to decrease as T^{-3}.

These predictions have not yet been subjected to an experimental test. The outer-sphere ET reaction for which the isotope effect can be explored should be characterized by an appreciable change in the metal–ligand distances, providing a large value for the reduced displacements, so that $E_c/\hbar\omega$ is large, resulting in large values for k_H/k_D. On the other hand, a large value for the reduced displacement of intramolecular vibrational modes might cause certain experimental difficulties in measuring the kinetics of ET, since these reactions are usually very slow. It is important to emphasize that deuterium isotope effects on outer-sphere ET reactions originate, in our opinion, from the quantum motion of the entire ligand with respect to the ion. Thus, the isotope effect originating from the replacement of a $H_2{}^{16}O$ molecule by a $D_2{}^{16}O$ molecule in the first coordination layer will practically be identical with the effect induced by substituting $H_2{}^{16}O$ by $H_2{}^{18}O$. Studies of these isotope effects should thus not be limited to deuteration but extended to the investigation of the consequences of $H_2{}^{16}O/H_2{}^{18}O$ and $^{14}NH_3/^{15}NH_3$ substitution on outer-sphere ET. Detailed experimental information is required concerning such isotope effects on a variety of ET processes studied in solutions and in glasses over a wide temperature range, in order to provide quantitative information concerning the role of quantum effects of nuclear tunneling on ET reactions.

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