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Electron Transfer

Insight into the Mechanism of the Ru^{2+}–Ru^{3+} Electron Self-Exchange Reaction from Quantitative Rate Calculations**

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Bimolecular reactions of the type given in Equation (1) (A,B = transition metal ions) have served as benchmarks for our theoretical understanding of electron transfer (ET) for the last fifty years.[1–16] Although experiments can quantify the kinetics and thermodynamics of such reactions rather accurately, it is theory, and more recently computation, that we have to rely on to gain insight into the mechanism and the rate-determining factors of ET reactions on a molecular scale. Indeed, many calculations have been carried out to estimate the ET parameters for reactions of the type given in Equation (1).[5,6,8–11,13–16] One important parameter characterizing such reactions is however still not well known, namely the most probable distance between the metal atoms A and B at which electron transfer occurs.

$$A^{2+}{}_{aq} + B^{3+}{}_{aq} \rightarrow A^{3+}{}_{aq} + B^{2+}{}_{aq} \qquad (1)$$

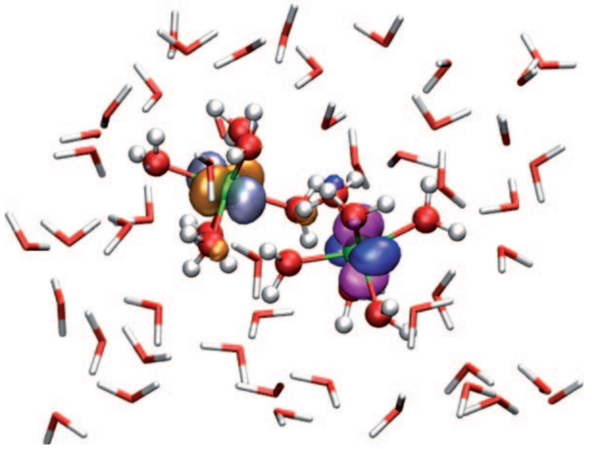

Figure 1. Snapshot of a molecular dynamics trajectory for the aqueous Ru^{2+}–Ru^{3+} ET complex. The HOMO of $[Ru(H_2O)_6]^{2+}$ is depicted in blue and purple, and the LUMO of $[Ru(H_2O)_6]^{3+}$ in gray and orange. Ru green, O red, H white.

Herein we investigate this important problem for the electron self-exchange reaction between $[Ru(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{3+}$ in aqueous solution (Figure 1). Using a multipronged approach that combines density functional theory (DFT) calculations, DFT-based and classical molecular dynamics (MD) simulation, and analytic theory, we show that it is possible to compute the rate of reaction Equation (1) without any adjustable parameter and with A = B = Ru almost quantitatively. From our calculations, we have determined the Ru–Ru distance for which the electron transfer rate is a maximum. The resultant value, 5.6 Å, is significantly smaller than the envelopes of the two hexahydrate complexes (7.1 Å). We find that the majority of ET events (> 99 %) occur in the range 4.9–8.0 Å, and that the rate drops nearly exponentially for distances outside this range.

The bimolecular ET reaction in Equation (1) may be viewed as a sequence of the following events: 1) diffusion of the solvated reactant complexes to form a (short-lived) ion-pair complex, 2) structural reorganization of the internal degrees of freedom of the reactant ion-pair complex and of the solvent molecules to form a configuration in which the initial (reactant) and final (product) diabatic ET states are degenerate (transition state), 3) electron transfer, 4) relaxation, and 5) dissociation of the product ion-pair complex. The theory we adopt herein to describe the kinetics of this reaction is based on the work of Newton and co-workers.[4] The reaction rate is expressed as the product of the probability for the two reactant complexes to approach one another at a metal–metal distance r, $\exp(-\beta G(r))$, and the intrinsic ET rate constant at this distance, $k_{ET}(r)$. Spherical integration gives the total reaction rate k:

$$k = 4\pi \int_0^\infty k_{ET}(r)\, e^{-\beta G(r)}\, r^2 dr = \int_0^\infty I(r) dr \qquad (2)$$

where $G(r)$ denotes the normalized potential of mean force for the two reactant complexes in solution and $\beta = (k_B T)^{-1}$, with T being the temperature and k_B the Boltzmann constant. For further reference, we have also introduced $I(r)$ on the right-hand side of Equation (2), the reaction rate within a spherical shell of thickness dr and at radius r. The first-order ET rate $k_{ET}(r)$ is approximated by the standard semiclassical expression of Marcus theory[1,2] multiplied by an enhancement factor k_q/k_{cl} that accounts for nuclear tunneling:[14]

$$k_{ET}(r) = \frac{2\pi}{\hbar} \langle |H_{ab}(r)|^2 \rangle \sqrt{\frac{\beta}{4\pi\lambda(r)}}\, e^{-\beta\lambda(r)/4}\, k_q/k_{cl} \qquad (3)$$

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where $H_{ab}(r)$ is the electronic coupling matrix element, $\lambda(r)$ is the reorganization free energy, $\hbar$ is Planck's constant divided by 2π, and $\langle\cdots\rangle$ denotes the thermal average. Equations (2) and (3) imply that the total rate constant and the most probable reaction distance, that is, the distance for which $I(r)$ is a maximum, can be readily obtained once the distance dependences of H_{ab}, λ, and G are known. We have calculated these values for the Ru^{2+}–Ru^{3+} electron self-exchange reaction. The details of the calculations are summarized in the Computational Methods, and the results are shown in Figure 2.

In Figure 2a, the electronic coupling matrix element H_{ab} averaged over an ensemble of transition state configurations of the $[Ru(H_2O)_6]^{2+}$–$[Ru(H_2O)_6]^{3+}$ ET complex is shown as obtained from DFT-based MD (see Figure 1). The distance dependence is almost perfectly exponential ($R^2 = 0.9998$) in the range 5.5–10.5 Å, $\langle |H_{ab}(r)| \rangle = A\exp(-\beta r/2)$, with a decay constant $\beta = 2.46$ Å^{-1}. The latter value is close to estimates for the isoelectronic ferrous–ferric electron self-exchange reaction.[5] The coupling is very sensitive to the thermal fluctuations of the ET complex, which is not surprising as H_{ab} is essentially determined by the overlap of the highest molecular orbital of $[Ru(H_2O)_6]^{2+}$ and the lowest unoccupied minority spin orbital of $[Ru(H_2O)_6]^{3+}$ (both are d orbitals of the t_{2g} manifold; see Figure 1). During the dynamics run, the orientation of the two orbitals fluctuates with the effect that the root-mean-square fluctuations of the coupling, $\sigma = (\langle |H_{ab}|^2\rangle - \langle |H_{ab}|\rangle^2)^{1/2}$ (shown as error bars in Figure 2a), are of the same order of magnitude as the average, $\sigma = 0.59\langle |H_{ab}|\rangle$, for $r = 5.5$ Å. The coupling calculated is for direct electron tunneling between the two hexahydrates. Contributions from superexchange were estimated by replacing the calculated rate of decay for distances larger than 7.5 Å by the experimental rate of decay for ET in liquid water, $\beta = 1.65$ Å^{-1}[18] (Figure 2a, –•–•). The effect of superexchange on the rate is, however, insignificantly small (Figure 2e, –•–•).

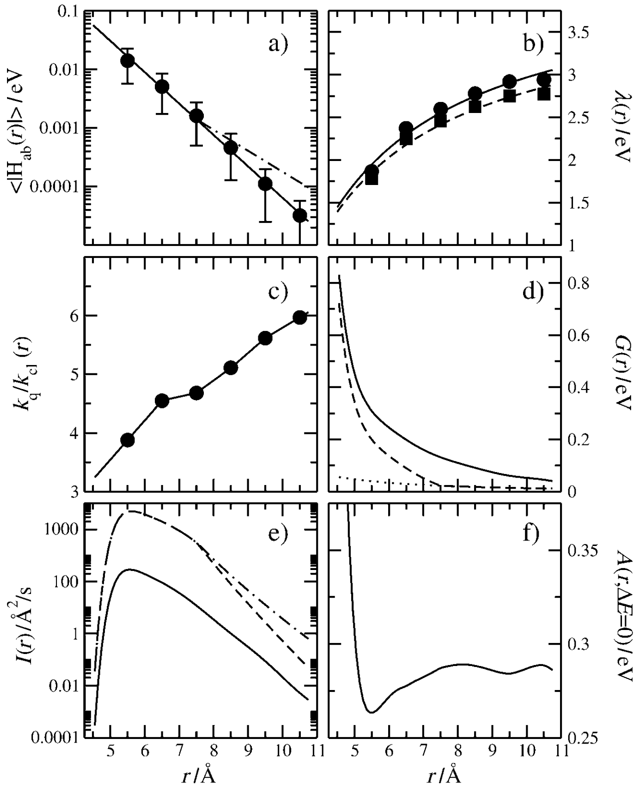

Figure 2. Distance dependences of ET parameters. a) Mean electronic coupling (●), exponential fit (——), superexchange correction for $r > 7.5$ Å (–•–•). b) Reorganization free energy for infinite dilution (●), for 5 M ionic strength (■), and fit functions (——). c) Quantum enhancement factor (●). d) Potential of mean force from MD simulation (——), mean electrostatic potential according to the Fuoss equation[17] for a solution of 5 M ionic strength (••••), and PMF replaced by the solution of the Fuoss equation for $r > 7.5$ Å (– – –). e) Distance-dependent reaction rate for infinite dilution (——), for 5 M ionic strength (– – –), and corrected for superexchange (–•–•). f) 1D cut of the 2D free-energy surface of Figure 3 along r at $\Delta E = 0$.

The reorganization free energy λ related to the activation free energy for ET ($\Delta G^{\neq} = 4\lambda$; see Equation (3)) is shown as a function of distance in Figure 2b. It was calculated as the sum of an inner-sphere contribution that arises from the two hexahydrate complexes and an outer-sphere contribution from the solvent. The distance dependence fits a curve of the form $a - b/r$ ($R^2 = 0.9995$) well, which is in agreement with the Marcus continuum formula.[1] The same dynamical data were used to calculate the nuclear quantum enhancement factor k_q/k_{cl} in the harmonic approximation[2] (Figure 2c). Finally, in Figure 2d we show the potential of mean force (PMF) G of the two hexahydrates in aqueous solution. For large distances, G decays like a screened Coulomb or Yukawa function, which has been used to normalize G; $\lim_{r\to\infty} G(r) = 0$. For short distances, $G(r)$ has been fitted to an eighth-order polynomial ($R^2 = 0.9998$).

With all the distance dependences available, the reaction rate within an infinitesimal spherical shell at distance r, $I(r)$, can be calculated (Figure 2e). For small distances, $I(r)$ is dominated by the repulsive short-range interactions of the water ligands (that is, by G). For large distances, $I(r)$ is dominated by the exponential decay of and to a lesser extent by the increasing λ. The opposing distance dependences of H_{ab} and λ on the one hand and of G on the other create a maximum for I at $r = 5.6$ Å. This value is somewhat larger than the estimate for the ferrous–ferric electron self-exchange reaction,[4] for which $r = 5.3$ Å. The difference accounts almost quantitatively for the larger metal–oxygen distances of the ruthenium complexes relative to the iron complexes.[3] Integration of $I(r)$ according to Equation (2) gives the total rate constant in the limit of infinite dilution, $k = 0.19$ dm^{3}mol^{-1}s^{-1}.

To compare to experimental values, we have to account for the fact that measurements have been carried out in acidic solutions of 5 M ionic strength. Extrapolation of the experimental rates to the infinite dilution limit was not possible because the ruthenium complexes decompose in neutral solutions.[19] As the reaction medium in experiment is composed of ions and counterions for which reliable force-field parameters are not readily available, we have used continuum theory to estimate the effect of the finite ionic strength on G and λ (see Computational Methods). We find that G is lowered for distances larger than 7.5 Å (dashed line in Figure 2d) as the counter ions screen the Coulomb repulsion between the ruthenium complexes. The reorganization free energy is also slightly lowered (Figure 2 b, ■) owing to the smaller static dielectric constant of the ionic solution. The overall effect of the finite ionic concentration is an increase in the rate $I(r)$ by two orders of magnitude (Figure 2 e, – – –) and an increase in the total rate from 0.19 to 37 $dm^3 mol^{-1} s^{-1}$. The latter value compares very well with the experimentally determined rate of 20 ± 4 $dm^3 mol^{-1} s^{-1}$.[19]

We are now in the position to investigate the mechanism of the Ru–Ru electron self-exchange reaction in more detail. For this purpose we constructed a two-dimensional free-energy surface of the reaction (Figure 3). One coordinate is the distance r, and the other is the vertical electron transfer energy ΔE, that is, the energy to transfer an electron from the donor to the acceptor complex at fixed nuclear configuration. The free energy is essentially a superposition of the two symmetric Marcus parabolae along ΔE and the potential of mean force G along r, namely $A(\Delta E,r) \approx (4\lambda(r))^{-1} \cdot (\Delta E - \lambda(r))^2 + G(r)$ for $\Delta E > 0$ and $A(-\Delta E,r) = A(\Delta E,r)$. Following the minimum free-energy path (thick red line in Figure 3), the two ruthenium complexes approach one another up to a distance of about 8.4 Å without a notable change in the ET coordinate ΔE. The latter decreases between 8.4 and 6 Å and strongly decreases between 6 and 5.5 Å. At $r = 5.5$ Å the two diabatic states are degenerate (transition state, $\Delta E = 0$) and ET occurs with a probability proportional to $|H_{ab}|^2$. Interestingly, the transition state along the minimum free-energy path is at a slightly smaller distance than the distance for which the rate $I(r)$ is a maximum (5.6 Å). The reason is that the entropic or surface term provides an additional weight factor of $4\pi r^2$ [see Eq. (2)] that is not included in the two-dimensional free-energy surface. The minimum free-energy path is not the only reactive path; in principle, ET can occur along the entire transition state line $\Delta E = 0$. However, a one-dimensional cut of $A(\Delta E,r)$ at $\Delta E = 0$ shows that there is only one sharp minimum at 5.5 Å (see Figure 2 f). The finite width of the minimum and the exponential decay of the coupling allow for significant ET to occur only in a small window between 4.9 and 8.0 Å. At these distances, the rate $I(r)$ has decayed to 1 % of its maximum value at 5.6 Å.

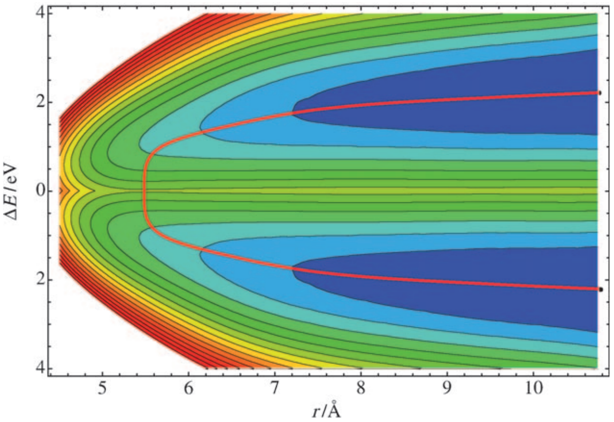

Figure 3. Free-energy surface $A(r,\Delta E)$ and the minimum free-energy path (thick red line) for the Ru^{2+}–Ru^{3+} electron self-exchange reaction in aqueous solution. Isolines for A are drawn every 0.08 eV from 0.08 eV (blue) to 1.24 eV (red).

To summarize, by using a combination of different computational techniques we have shown that it is possible to calculate the total reaction rate of the aqueous Ru^{2+}–Ru^{3+} electron self-exchange reaction in very good agreement with experiment. The calculations provided for the first time an estimate for the rate in the limit of infinite dilution and showed that the high ionic concentration in experiment leads to an increase in the reaction rate by two orders of magnitude. The atomistic resolution of our calculations have allowed us to obtain a molecular picture of this reaction at an unprecedented level of detail. In particular, our calculations confirm previous suggestions[4,8,11] that the ET reaction occurs at distances that are significantly smaller than the envelopes of the two encounter complexes.

Computational Methods

Electronic coupling matrix elements were calculated using a fragment orbital DFT (FO-DFT) approach[20] implemented in the Car-Parrinello MD code (CPMD[21]). First, an ab-initio MD simulation was carried out for a periodic box of dimensions $14.5 \times 11.35 \times 11.35$ Å^3 containing two ruthenium ions constrained at a distance of 5.5 Å and 63 water molecules per unit cell. 450 equidistantly spaced snapshots of the $[Ru(H_2O)_6]^{2+}$–$[Ru(H_2O)_6]^{3+}$ ET complex were then extracted from the MD trajectory and embedded in a large vacuum box for the FO-DFT calculation. The neglect of effects of the second and higher solvation shells on the electronic coupling was shown to be a good approximation for the reaction investigated in Ref. [22], and this was in fact also assumed in recent[16] and earlier studies of ET reactions.[4] Calculations of the coupling matrix elements for larger Ru–Ru distances were carried out for the same ensemble of snapshots with the $[Ru(H_2O)_6]^{3+}$ complex translated along the Ru–Ru axis to the desired distance. The BLYP[23,24] functional was used with a plane-wave cutoff of 70 Ry and pseudopotentials as described in Ref. [25].

The outer-sphere contributions to λ and to k_q/k_{cl} were obtained from MD simulation as described in Ref. [14] for Ru–Ru distances constrained to values ranging from 5.5 to 10.5 Å. Each unit cell contained two ruthenium ions and 1022 (polarizable) POL3 water molecules.[26] Finite size effects of λ owing to the limited number of water molecules were found to be negligible for this system size.[14] The inner-sphere contribution to λ was taken from Ref. [14]. $G(r)$ was obtained from umbrella sampling of the same 1022 water-molecule system by dividing the range of distances into six individual strata, each of which was biased to compensate for the effect of the Coulomb repulsion of the two hexahydrates. The fairly good decay of $G(r)$ towards zero shows that the simulation box was chosen sufficiently large.

Details on the force-field parameters of the ET complex can be found in Ref. [14]. All classical simulations were carried out with the AMBER9 simulation package.[27] The reorganization free energy at finite ionic concentration was estimated by multiplying the reorganization free energy calculated for infinite dilution with the ratio of Pekar factors of a pure aqueous solution and of a solution 5 M in ionic strength. We have adopted the optical (ε_{op}) and static dielectric constants (ε_s) of a 5 M NaCl solution for this purpose.[28] $\lambda_{salt}(r) = \lambda(r)[\varepsilon_{op}^{-1}(\text{salt}) - \varepsilon_s^{-1}(\text{salt}) / \varepsilon_{op}^{-1}(H_2O) - \varepsilon_s^{-1}(H_2O)]$. To account for the effect of ionic strength on $G(r)$, the calculated PMF was replaced for distances larger than 7.5 Å by the mean-force potential predicted according to the Fuoss equation.[17] The switching parameter corresponds to a distance at which one chloride counter ion fits between the two hexahydrates. The results are not sensitive to the precise value of this parameter, however.

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