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The Kinetics of the Oxidation of Metal Complexes by Hexakis(urea)manganese(III) in Acetonitrile

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Abstract

The kinetics of the outer-sphere reduction of the hexakis(urea)manganese(III) ion by a series of nickel(II) macrocycles and metal(II) tris(polypyridine) complexes have been investigated in acetonitrile at 25 °C. The electron self-exchange rate constant for the $Mn(urea)_6^{2+/3+}$ couple has been derived from the cross-reaction kinetic data using the Marcus relationship and calculated using a semi-classical model. The rate constant derived from the cross-reactions with the nickel macrocycle complexes is in reasonable agreement with the value calculated from the semi-classical model, at 10^{-1} M^{-1} s^{-1}. A range of much lower self-exchange rate constants, 10^{-5}–10^{-2} M^{-1} s^{-1}, results from the cross-reactions of $Mn(urea)_6^{3+}$ with the metal(II) tris(polypyridine) complexes. The discrepancies in the rate constants are discussed in terms of the degree of nonadiabaticity in the cross-reactions, and its relationship to the nature of the substituents on the polypyridine complexes. The self-exchange rate constant for $Mn(urea)_6^{2+/3+}$ is compared with those of other Mn(II)/Mn(III) couples and related to the reorganization barriers to electron exchange.

Introduction

Experimental and theoretical investigations of electron-exchange reactions of transition metal complexes have demonstrated the relationship between the nature of the donor–acceptor orbital (dπ or dσ^*) and the magnitude of the exchange rate constants [1, 2]. For complex couples where the transferring electron resides in an antibonding dσ^* orbital, such as for $Cr(H_2O)_6^{2+/3+}$, a large difference (~0.20 Å) between the M–O bond distances of the reduced and oxidized forms results in a very slow rate of electron-exchange ($k_{11} < 2 \times 10^{-5}$ M^{-1} s^{-1}) [3]. Electron exchange in the $Mn(H_2O)_6^{2+/3+}$ couple, involving the transfer of a dσ^* electron and a similar inner-sphere configuration change (~0.19 Å), has recently been investigated [4]. The exchange rate constant derived from a series of outer-sphere cross-reactions with $Mn(H_2O)_6^{3+}$ varied from 10^{-9}–10^{-3} M^{-1} s^{-1} depending on the nature of the reductant. An outer-sphere semi-classical model predicts a rate constant of $10^{-4\pm1}$ M^{-1} s^{-1} as a result of the significant reorganization of the Mn–O bond distances. Very few Mn(II)/Mn(III) exchange rate constants have been determined [4, 5] and to further investigate electron exchange in this metal system, other complexes containing monodentate oxygen donor ligands were sought for kinetic studies.

The hexakis(urea)manganese(III) ion is easily prepared as a perchlorate salt and, although sensitive to water, is reasonable stable in anhydrous acetonitrile. The recently reported molecular structure of the complex [6] indicates the presence of a dynamic Jahn–Teller effect, with equivalent Mn–O bond distances in this high-spin d^4 cation. In this paper the results of a kinetic study of the reduction of the hexakis(urea)manganese(III) ion by a series of metal complexes in acetonitrile are reported. The electron self-exchange rate constant for the $Mn(urea)_6^{2+/3+}$ couple is estimated from the cross-reaction kinetic data and also calculated by means of a semi-classical model. The electron exchange rate for this couple is compared with other Mn(II)/Mn(III) systems, and discussed in terms of the solvent and inner-sphere reorganization barriers involved.

Experimental

Materials

Hexakis(urea)manganese(III) perchlorate [6] and hexakis(urea)manganese(II) perchlorate [7] were prepared by published procedures. The tris(polypyridine) complexes, $[ML_3]^{2+}$, where M is osmium(II), iron(II), or ruthenium(II), and L is 2,2'-bipyridine, 1,10-phenanthroline, or a derivative of bpy or phen, were prepared as chloride or perchlorate salts as described previously [8, 9]. The nickel(II) macrocyclic compounds; $[Ni([14]aneN_4)](ClO_4)_2$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) [10], $[Ni([9]aneN_3)_2](ClO_4)_2$ ($[9]aneN_3$ = 1,4,7-

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triazacyclononane) [11], [Ni(Me$_2$[14]dieneN$_4$)]-(ClO$_4$)$_2$ (Me$_2$[14]dieneN$_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclodeca-4,11-diene) [10], were prepared as reported previously. Acetonitrile (HPLC grade, Fisher) was dried and distilled from calcium hydride. Tetrabutylammonium perchlorate (Eastman) was dried under reduced pressure at 80 °C.

Kinetic Measurements

The kinetic studies of the oxidation of metal complexes by Mn(urea)$_6^{3+}$ were performed using the TDI Model IIA stopped-flow apparatus (Cantech Scientific) and data acquisition system described previously [12]. The reactions were monitored at 400 nm for the nickel macrocycles and at 460–520 nm for the metal tris(polypyridine) complexes. Pseudo-first-order conditions of excess Mn(urea)$_6^{3+}$ over reductant concentrations (1–3 X 10^{-5} M) were employed and plots of $\ln(A_\infty - A_t)$ or $\ln(A_t - A_\infty)$ against time were observed to be linear for at least three half-lives. The reactant solutions were prepared in dry acetonitrile containing 0.10 M tetrabutylammonium perchlorate (TBAP). The kinetic measurements were performed at 25.0 ± 0.1 °C, with thermostatting provided by an external water bath.

Results

The stoichiometry of the reactions between hexakis(urea)manganese(III) and the metal complexes used as reductants in this study were determined by spectrophotometric titrations in acetonitrile containing 0.10 M TBAP. The ratio of moles of reductant consumed per mole of Mn(urea)$_6^{3+}$ was found to be (1.0 ± 0.05):1.0 for each type of metal complex, indicating the general overall reaction in eqn. (1).

$$\mathrm{Mn(urea)_6^{3+}} + \text{Reductant} \longrightarrow \mathrm{Mn(urea)_6^{2+}} + \text{Oxidant} \qquad (1)$$

The kinetics of the reactions between Mn(urea)$_6^{3+}$ and a series of nickel(II) polyaza macrocycles and metal(II) tris(polypyridine) complexes were studied at 25.0 °C in acetonitrile (0.10 M TBAP). Pseudo-first-order conditions of excess oxidant concentrations were employed and the observed first-order rate constants displayed linear dependences on the concentration of Mn(urea)$_6^{3+}$.

$$\frac{-\mathrm{d}[\text{Red.}]}{\mathrm{d}t} = k_{\text{obsd}}[\mathrm{Mn(urea)_6^{3+}}][\text{Red.}] \qquad (2)$$

The second-order rate constants, k_{12}, for the cross-reactions in this study are presented in Table 1.

Discussion

In the absence of a direct measurement of the electron exchange rate constant for a transition metal

TABLE I. Cross-reaction Rate Constants for the Oxidation of Metal Complexes by Mn(urea)$_6^{3+}$ in Acetonitrile at 25.0 °C (0.10 M TBAP)

No.	Reductant	$\ln K_{12}$	k_{12} ($M^{-1}\,s^{-1}$)	k_{22} [a] ($M^{-1}\,s^{-1}$)	k_{11} [b] ($M^{-1}\,s^{-1}$)
1	Ni(Me$_2$[14]4,11-dieneN$_4$)$^{2+}$	5.06	2.92×10^2	3.0×10^3	1.9×10^{-1}
2	Ni([14]aneN$_4$)$^{2+}$	7.01	5.09×10^2	2.0×10^3	1.4×10^{-1}
3	Ni([9]aneN$_3$)$_2^{2+}$	7.39	1.21×10^3	6.0×10^3	1.9×10^{-1}
4	Os(5-Clphen)$_3^{2+}$	8.17	4.77×10^4	8.0×10^7	6.2×10^{-3}
5	Os(bpy)$_3^{2+}$	12.4	1.68×10^5	5.0×10^7	4.1×10^{-3}
6	Os(phen)$_3^{2+}$	12.4	1.74×10^5	8.0×10^7	2.8×10^{-3}
7	Os(5-CH$_3$phen)$_3^{2+}$	13.6	1.95×10^5	9.0×10^7	8.5×10^{-4}
8	Os(4,4′-(C$_6$H$_5$)$_2$bpy)$_3^{2+}$	15.2	7.10×10^4	8.0×10^7	2.3×10^{-4}
9	Os(4,7-(C$_6$H$_5$)$_2$phen)$_3^{2+}$	15.6	1.14×10^5	9.0×10^7	3.7×10^{-4}
10	Os(5,6-(CH$_3$)$_2$phen)$_3^{2+}$	15.6	3.15×10^5	1.0×10^8	2.8×10^{-4}
11	Os(4,4′-(CH$_3$)$_2$bpy)$_3^{2+}$	16.8	1.10×10^5	5.0×10^7	2.4×10^{-5}
12	Fe(bpy)$_3^{2+}$	3.50	7.47×10^2	9.0×10^6	1.4×10^{-3}
13	Fe(4,7-(C$_6$H$_5$)$_2$phen)$_3^{2+}$	5.84	8.54×10^2	3.0×10^7	1.7×10^{-5}
14	Fe(5,6-(CH$_3$)$_2$phen)$_3^{2+}$	6.61	1.84×10^3	2.0×10^7	1.2×10^{-4}
15	Fe(4,4′-(CH$_3$)$_2$bpy)$_3^{2+}$	8.56	3.39×10^3	2.0×10^7	6.7×10^{-5}
16	Fe(4,7-(CH$_3$)$_2$phen)$_3^{2+}$	10.5	4.50×10^3	3.0×10^7	1.4×10^{-5}
17	Fe(3,4,7,8-(CH$_3$)$_4$phen)$_3^{2+}$	12.8	1.00×10^4	4.0×10^7	4.4×10^{-6}
18	Ru(4,7-(CH$_3$)$_2$phen)$_3^{2+}$	1.95	8.15×10^2	1.0×10^8	3.8×10^{-4}
19	Ru(3,5,6,8-(CH$_3$)$_4$phen)$_3^{2+}$	1.95	5.02×10^2	1.0×10^8	1.4×10^{-4}
20	Ru(3,4,7,8-(CH$_3$)$_4$phen)$_3^{2+}$	4.67	1.50×10^3	1.0×10^8	5.7×10^{-5}

[a] Self-exchange rate constants for Ni(II)/Ni(III) macrocycles from ref. 13, for ML$_3^{2+/3+}$ from ref. 14 (see text). [b] Self-exchange rate constant for Mn(urea)$_6^{2+/3+}$ calculated using eqn. (4).

complex couple, such as $Mn(urea)_6^{2+/3+}$, estimates may be obtained from semi-classical model calculations [2], or from the application of the Marcus relationship [15] to kinetic data from a series of cross-reactions involving the couple. In the semi-classical model the self-exchange rate constant of a couple, k_{11}, may be expressed as the product of a pre-equilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors, κ_{el} and κ_n [2]. The nuclear factor is given by eqn. (3)

$$\kappa_n = \Gamma_n \exp[-(\Delta G^*_{in} + \Delta G^*_{out})/RT] \qquad (3)$$

where Γ_n is a nuclear tunnelling factor and ΔG^*_{in} and ΔG^*_{out} are the inner-sphere and solvent reorganization energies, respectively.

The inner-sphere reorganization energy, required to change the nuclear configurations of the reactants to a common state prior to electron transfer, is a function of the bond length differences (Δd_o) in the two oxidation states and the reduced force constants associated with breathing mode vibrations of the bonds. The $Mn(urea)_6^{2+/3+}$ exchange reaction involves the transfer of an electron from a high-spin d^5 $[(d\pi)^3(d\sigma^*)^2]$ configuration of Mn(II) to a high-spin d^4 $[(d\pi)^3(d\sigma^*)^1]$ configuration of Mn(III). As the electron exchange involves orbitals of antibonding character, a change in their population should be accompanied by a considerable change in the Mn–O bond distances. While the Mn–O bond distance in a complex containing the $Mn(urea)_6^{2+}$ ion has not been determined, the Mn–O bond distance for the axial dimethylureas in $Mn(dimethylurea)_3Br_2$ is 2.175 Å [16], within the range of 2.16–2.18 Å observed in a number of Mn(II) complexes containing oxygen donor ligands (e.g. H_2O [17], lactate [18]). The Mn–O distance for a Mn(II)–urea bond is taken to be 2.17 ± 0.01 Å. The Mn–O bond distance in the $Mn(urea)_6^{3+}$ ion has been reported to be 1.99 Å in $[Mn(urea)_6](ClO_4)_3$ [6]. With the high-spin d^4 electronic configuration, the $Mn(urea)_6^{3+}$ ion should be susceptible to a Jahn–Teller distortion of the Mn–O distances. The six identical Mn–O bonds and other spectroscopic data [6] are indicative of a dynamic Jahn–Teller effect. The difference in the manganese–oxygen bond distances, Δd_o, is therefore 0.18 ± 0.01 Å. The reduced force constant for the Mn–O bonds in the $Mn(urea)_6^{2+/3+}$ couple is assumed to be similar to that in the $Mn(H_2O)_6^{2+/3+}$ couple [4] and taken to be 200 N m^{-1}. Using these values ΔG^*_{in} is calculated to be 14.0 ± 1.5 kcal mol^{-1}.

The magnitude of the energy required to reorient the solvent prior to electron transfer, ΔG^*_{out}, is a function of the nature of the solvent and the sizes and separation distance of the complexes. Using the dielectric continuum expression for ΔG^*_{out} [15], a value of 4.1 kcal mol^{-1} is calculated for the $Mn(urea)_6^{2+/3+}$ couple (radius of $Mn(urea)_6^{n+}$ is 5.5 Å) in acetonitrile. After including the nuclear tunneling correction ($\Gamma_n = 3.1$) [2], the nuclear factor is calculated to be 1.4×10^{-13}. The nuclear frequency ν_n is related to the inner-sphere and solvent reorganization terms; $\nu_n = [(\nu_{out}^2\Delta G^*_{out} + \nu_{in}^2\Delta G^*_{in})/(\Delta G^*_{out} + \Delta G^*_{in})]^{1/2}$. For $Mn(urea)_6^{2+/3+}$ ν_n is calculated to be 7.8×10^{12} s^{-1}, using $\nu_{out} = 4.5 \times 10^{12}$ s^{-1} (solvent reorientation frequency for acetonitrile [19]) and $\nu_{in} = 8.6 \times 10^{12}$ s^{-1}. With a pre-equilibrium constant $K_A = 0.09$ M^{-1}, the semi-classical model predicts an adiabatic ($\kappa_{el} = 1$) exchange rate constant of $1 \times 10^{-1 \pm 1}$ M^{-1} s^{-1} for the $Mn(urea)_6^{2+/3+}$ couple. The calculations above are based on a two-sphere model of the precursor and successor complexes in which the separation distance of the metal centers is the sum of the hard-sphere radii of the reactants. An alternative ellipsoidal model would allow for some interpenetration of the inner-coordination spheres [2], however this would affect K_A and ΔG^*_{out} in a manner which would tend to cancel the effect of each other on k_{11}. The $Mn(urea)_6^{2+/3+}$ exchange rate constant is approximately 10^3 larger than the value determined for the $Mn(H_2O)_6^{2+/3+}$ couple using the same model. The difference arises primarily from a lower solvent reorganization barrier associated with the larger urea complex.

The cross-reaction kinetic data from this study may be correlated in terms of a recent modification of the Marcus relationship [2], which relates the rate constant for a cross-reaction k_{12} to the rate constant for the component self-exchange reaction k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (4)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\dfrac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \dfrac{w_{11} + w_{22}}{RT}\right]} \qquad (5)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (6)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{1/2})} \qquad (7)$$

In the above expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of the radii of the ions), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, and $A_{ii} = (4\pi N\sigma^2\nu_n(\delta r)/1000)_{ii}$, where δr is the thickness of the reaction shell (~0.8 Å [2]). The values of σ_{ij} used in the calculations are based on radii of 5.5 Å for $Mn(urea)_6^{n+}$ and the nickel macrocycle complexes, and 6.8–11.6 Å for the substituted $M(bpy)_3^{n+}$ and $M(phen)_3^{n+}$ complexes. The reduction potential

($vs.$ NHE) for $Mn(urea)_6^{3+}$ in acetonitrile is 1.14 V [20]. The reduction potentials of the Ni(III) macrocycles [13] and the tris(polypyridine) complexes of Os(III), Fe(III), and Ru(III) [9, 21] are taken from reported values in acetonitrile or extrapolated using potentials measured in aqueous media. The self-exchange rate constants for many of the reductant couples (Table I) have been determined by either direct measurements or from the application of the Marcus relationship to cross-reactions involving the reductants. For the metal tris(polypyridine) couples for which k_{22} has not been measured, the exchange rate constant was estimated from the available data for $ML_3^{2+/3+}$ couples and the observed dependences of k_{22} on the nature of M and L [14].

The $Mn(urea)_6^{2+/3+}$ self-exchange rate constants, k_{11}, calculated from each of the cross-reactions using eqn. (4), are presented in Table I. The cross-reactions involving the nickel(II) macrocycles yield values of 0.1–0.2 M^{-1} s^{-1}, which are in reasonably good agreement with the rate constant predicted by the semi-classical model for this couple. From the cross-reactions with the metal polypyridine complexes, however, much lower (10^{-5}–10^{-2} M^{-1} s^{-1}) and less consistent values of k_{11} are obtained. The variation in k_{11} may also be seen in the Marcus correlation in Fig. 1, where the magnitude of k_{11} appears to depend on both the nature of the metal and the substituted polypyridine ligand. The apparent non-adiabaticity of these cross-reactions; $(\kappa_{el})_{12} \ll ((\kappa_{el})_{11}(\kappa_{el})_{22})^{1/2}$, has also been observed in numerous other electron transfer reactions involving these metal polypyridine species, including those with the $Mn(H_2O)_6^{3+}$ ion [4]. Electron exchange in couples such as $Ru(bpy)_3^{2+/3+}$ is believed to proceed primarily by overlap of stacked bipyridine rings as there is significant delocalization of metal dπ electron density onto the ligand π^* orbitals [9]. In the cross-reactions of these complexes with the $Mn(urea)_6^{3+}$ ion, however, the respective π^*–π^* and d–d electron exchange pathways are not compatible and electron transfer likely occurs through ineffective d–d overlap between the metal centers. The d–d overlap between $Mn(urea)_6^{3+}$ and ML_3^{2+} should be enhanced somewhat as the metal changes from Fe (3d) to Ru (4d) to Os (5d) as a result of greater radial extension of the t_{2g} orbital. This effect may be seen in the ranges of k_{11} derived from each metal system, with $OsL_3 > RuL_3 > FeL_3$ in general. Effective overlap would be reduced, however, when substitution of the ligands with methyl and phenyl groups leads to an increase in the Mn–M separation distance. The lowest derived k_{11} values come from cross-reactions involving the tetramethyl and diphenyl derivatives.

In addition to the $Mn(urea)_6^{2+/3+}$ couple there are very few Mn(II)/Mn(III) systems for which an electron exchange rate constant has been measured or estimated. For the $Mn(H_2O)_6^{2+/3+}$ [4] and Mn(edta)-$(H_2O)^{2-/-}$($edta^{4-}$ = ethylenediaminetetraacetate) [5, 22] self-exchange rate constants of 10^{-4} M^{-1} s^{-1} and 1.2 M^{-1} s^{-1}, respectively, have been determined. These three couples have high-spin d^5/d^4 electronic configurations, leading to large differences in Mn(II)–L and Mn(III)–L bond lengths and sizable inner-sphere reorganization barriers. The differences in k_{11} for these couples, on the basis of semi-classical model calculations originate in the respective pre-equilibrium constants and solvent reorganization energies. Kinetic studies are in progress [22] on cross-reactions of other Mn(II)/Mn(III) couples in order to extend these comparisons.

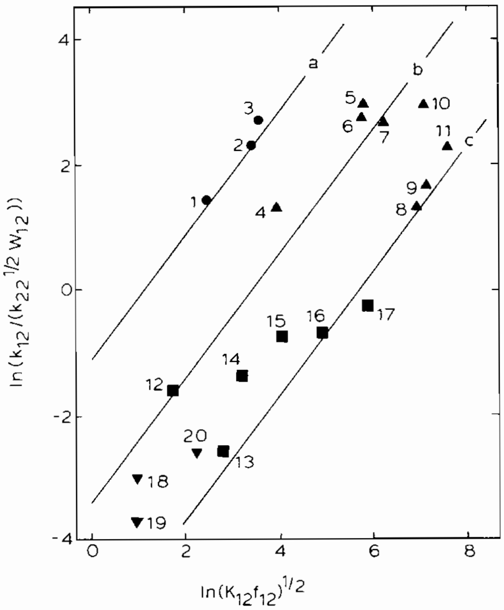

Fig. 1. Plot of $\ln(k_{12}/(k_{22}^{1/2}W_{12}))$ against $\ln(K_{12}f_{12})^{1/2}$ for the oxidation of metal complexes by $Mn(urea)_6^{3+}$. The reductants; (●) Ni(II) macrocycles, (▲) OsL_3^{2+}, (■) FeL_3^{2+}, and (▼) RuL_3^{2+}, are numbered as in Table I. The solid lines represent the theoretical slope of unity corresponding to k_{11} ($Mn(urea)_6^{2+/3+}$) values of (a) 10^{-1} M^{-1} s^{-1}, (b) 10^{-3} M^{-1} s^{-1}, and (c) 10^{-5} M^{-1} s^{-1}.

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