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A Model for the Prediction of the Molar Volume Effects Accompanying Changes in the Primary Coordination Number of Aqueous Metal Ions

Sir:

Despite extensive recent discussion,[1-12] the question of the limiting values of the volume of activation ΔV^* that can be expected for ligand substitution on metal cations according to extreme associative or dissociative mechanisms remains unsettled. This is hardly surprising, since the central problem is prediction of the molar volume of complexes of expanded or reduced primary coordination number n that are usually not amenable to direct observation. In this paper, an alternative approach to the problem, using the semiempirical equation (1),[13] is proposed.

$$\bar{V}^0_{\mathrm{abs}}/\mathrm{cm^3\ mol^{-1}} = 2.523 \times 10^{-6}(r + 238.7)^3 - 18.07n - 417.5z^2/(r + 238.7) \qquad (1)$$

Equation 1 relates the "absolute" partial molar volume $\bar{V}^0_{\mathrm{abs}}$ (at infinite dilution, 298 K and 0.1 MPa, relative to $\bar{V}^0_{\mathrm{abs}} = -5.4$ cm³ mol⁻¹ for aqueous H^+ [14]) of an aqueous cation M^{z+} of effective ionic radius[15] r (in pm) to n. We have shown elsewhere[8,13] that eq 1 reproduces measured $\bar{V}^0_{\mathrm{abs}}$ values for aqueous M^{z+} for which n is known (e.g., from NMR or X-ray diffraction studies of solutions) to within 2 $\mathrm{cm^3\ mol^{-1}}$ in almost all cases, that is, to within the experimental uncertainty of the data for many ions of $z > 1$ at least.

It transpires that this approach can also account satisfactorily for the difference between the volumes of activation for outer-sphere and inner-sphere alternative pathways for electron transfer between aqueous metal cations.

Previous Models. Stranks[16] suggested that the first coordination "spheres" of species ML_n^{z+} could be approximated to real spheres from the point of view of the volume swept out by ML_n^{z+} in solution and that this volume (and hence the measured molar volume of ML_n^{z+}) should be the same for given M, L, and z whether n were 5 or 6. Thus, for the dissociative activation process

$$ML_6^{z+} \rightarrow \{ML_5^{z+}\}^* + L \qquad (2)$$

the limiting value of ΔV^* would be the molar volume V_L of L, while for associative activation of ML_6^{z+}

$$ML_6^{z+} + L \rightarrow \{ML_7^{z+}\}^* \qquad (3)$$

ΔV^* could range down to $-V_L$. In fact, ΔV^* for solvent-exchange reactions (L = solvent) does not approach $\pm V_L$ even remotely,[3] while arguments advanced[19] to support the claim that the molar volumes of $Co(NH_3)_6^{3+}$ and the hypothetical intermediate $Co(NH_3)_5^{3+}$ are effectively the same in aqueous solution have been discredited in two independent studies.[4,6] Stranks' hypothesis as originally formulated[16] must necessarily fail because the implicit assumption, that the apparent ionic radius r (and hence the effective radius of the quasi-spherical complex ML_n^{z+}) is independent of the coordination number n, is substantially in error, as the compilation of Shannon[15] clearly shows. This point has been made in various forms by several authors, most notably Langford,[9,11,17,18] and indeed the success of eq 1 in reproducing experimental $\bar{V}^0_{\mathrm{abs}}$ data is dependent upon use of the appropriate value of r for the relevant n.[13] The model proposed in the next section may be regarded as an attempt to correct Stranks' model for the interdependence of r and n.

Table I. Limiting Volumes of Activation for Water Exchange on Octahedral Aqua Cations at 298 K, Calculated from Eq 1 by Using Shannon's[15] Effective Ionic Radii

	limiting ΔV^*/cm³ mol⁻¹			limiting ΔV^*/cm³ mol⁻¹	
M^{z+}(aq)	dissociative	associative	M^{z+}(aq)	dissociative	associative
$Na^{+\,a}$	13.6[b]	−11.7[b]	Cu^{2+}	12.2	
Mg^{2+}	13.7		Zn^{2+}	13.6	
Al^{3+}	14.3		Ga^{3+}	13.1	
Mn^{2+}	11.8	−12.4	$Y^{3+\,a}$		−12.9
Mn^{3+}	13.4		Ag^+	12.5	−11.3
Fe^{3+}	13.4		Cd^{2+}	11.4	−11.0
Co^{2+}	12.5		$U^{4+\,a}$		−12.7
Ni^{2+}	13.7				

[a] Assumed six coordinate in water. [b] Calculated from $r = 105$ pm for $n = 6$ (Table 4 of ref 15).

An alternative approach[3,7,8,11] to the establishment of outer limits to ΔV^* for water exchange on $M(H_2O)_6^{z+}$ takes the water molecule to be a sphere of radius 138 pm and notes that, when $r \sim 57$ pm (close to the values observed for several M^{3+}), the six water ligands are effectively closest packed around M. It is then easy to calculate that the upper limit to ΔV^* for dissociative water loss would be +9.1 cm³ mol⁻¹, which seems reasonable. This model, however, ignores covalent interactions between M^{z+} and the water ligands and again assumes r to be independent of n (although this is not directly relevant to the model). Furthermore, the ligands in most $M(H_2O)_6^{2+}$ entities cannot be said to be closest packed. More seriously, the model does not readily allow prediction of ΔV^* for *associative* water exchange (eq 3) except to suggest that it should be no more negative than −9.1 cm³ mol⁻¹ by (false) analogy with the reverse of the dissociative process. In fact, ΔV^* for water exchange on $V(H_2O)_6^{3+}$ is now known to be about −10.1 cm³ mol⁻¹.[20] Thus, the "closest packing" model apparently underestimates the limiting values of $|\Delta V^*|$ for water exchange, at least where associative activation seems to be operative.

Model Based on Eq 1. The three terms on the right-hand side of eq 1 represent respectively (i) the volume of 1 mol of quasi-spherical complexes $M(H_2O)_m^{z+}$ of radii $(r + \Delta r)$, where Δr is an adjustable parameter (evaluated to be 238.7 ± 0.7 pm) that accommodates the contribution of packing voids and the unknown distance of closest approach of electrostricted solvent, (ii) the loss of the contributions of the n water molecules (now covered by term i) to the volume of the free solvent, and (iii) the Born–Drude–Nernst electrostrictive effect of $M(H_2O)_n^{z+}$ on solvent beyond $(r + \Delta r)$, which may be

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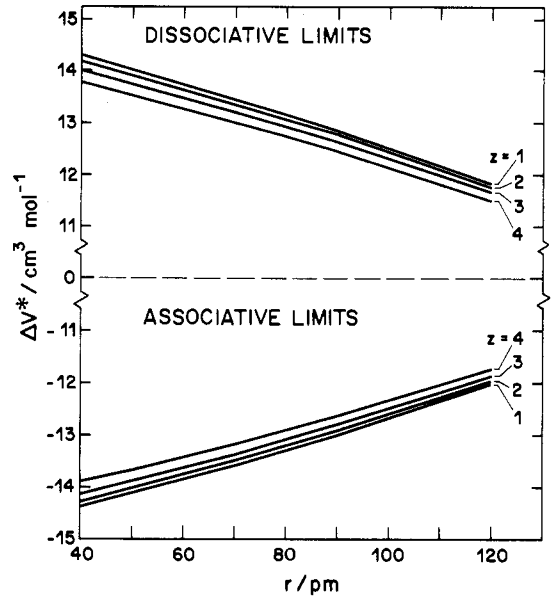

Figure 1. Limiting volumes of activation for dissociative and associative water exchange on 6-coordinate aqueous ions M^{z+} as functions of the Shannon crystallographic ionic radii *r*.

treated as a continuous dielectric.[13] If *r* were independent of *n*, the volume change for the dissociative process

$$M^{z+}(\text{aq}, n\text{-coordinate}) \rightarrow M^{z+}(\text{aq}, (n-1)\text{-coordinate}) \quad (4)$$

would be +18.07 cm³ mol⁻¹ and that for the associative process

$$M^{z+}(\text{aq}, n\text{-coordinate}) \rightarrow M^{z+}(\text{aq}, (n+1)\text{-coordinate}) \quad (5)$$

would be −18.07 cm³ mol⁻¹, according to eq 1, which would correspond to the prediction of Stranks' model.[16]

In general, however, *r* increases markedly with *n*, and Table I lists volume changes for prcesses 4 and 5 (representing the outer limits of ΔV^* for water exchange) for a variety of 6-coordinate aqueous M^{z+} for which Shannon[15] provides *r* values for $n = 5$ and/or 7 as well as 6. Alternatively, we may use an average of the differences δr between Shannon's *r* values[15] for 6- and 5-coordination and for 6- and 7-coordination, since δr shows no correlation with the actual magnitude of *r*. The averages of δr are −6.5 ± 2.1 pm for process 4 and +6.1 ± 1.7 pm for process 5, and these values generate the families of curves representing the extremes of the range of ΔV^* for aqua exchange shown in Figure 1.

The limiting ΔV^* values of Table I are individually rather imprecise, since Δr is subject to ~20% uncertainty, but they conform generally to the following trends, which are discernible in Figure 1. (a) The limiting values of $|\Delta V^*|$ for aqua exchange are predicted to be almost independent of the ionic charge per se, being only some 0.5 cm³ mol⁻¹ smaller for 4+ than for 1+ ions of the same radius. (b) The limiting $|\Delta V^*|$ is about the same for associative as for dissociative processes for a given ion—a conclusion that was not readily drawn from the "closest packing" model. (c) $|\Delta V^*|$ decreases as the ionic radius increases whatever the mechanism, but even in the limit this effect amounts to only ~1.6 cm³ mol⁻¹ for the normal range in *r* for octahedral aqua complexes; the limits of $|\Delta V^*|$ amount to ~13.5 cm³ mol⁻¹ for typical M^{3+} such as Fe^{3+} and ~13.1 cm³ mol⁻¹ for M^{2+} such as Fe^{2+}. (d) The limiting $|\Delta V^*|$ values are markedly smaller than the 18.1 cm³ mol⁻¹ predicted by Stranks' hypothesis and exceed the largest measured $|\Delta V^*|$ values by an amount close to that (2.5–3.0 cm³ mol⁻¹)[7] expected if the water-exchange process involves the primary coordination sphere and the rest of the solvation sheath but *not* bulk solvent directly—that is, if the intermediates of processes 4 and 5 are short-lived relative to diffusion between bulk solvent and the solvation sheath (an interchange mechanism), as will usually be the case.

In connection with point d, we note that the difference in $\bar{V}^0_{\text{abs}}$ for 8- and 9-coordinate forms of aqueous lanthanoid(III) ions does indeed seem to be about 13 cm³ mol⁻¹.[13] Further, the differences between the molar volumes of bulk water and averaged-out electrostricted water calculated by Stranks[16] (3.0 cm³ mol⁻¹ for the second coordination sphere, 2.4 for the presumed third) are in close agreement with quasi-experimental values[7] but were associated with the wrong electrostatic pressures in the original article[16] and in a recent review;[1] molar volumes of 15.0 and 15.6 cm³ mol⁻¹ for water at 298 K correspond to pressures of 750 and 514 MPa, respectively,[21] not 3.2 GPa and 750 MPa as reported.[1,16] Water assumes the form of ice-VII (molar volume ≤10.9 cm³ mol⁻¹)[22] at 298 K and 3.2 GPa, which seems a resonable estimate of the average electrostatic pressure acting on the *primary* coordination sphere.

Inner- vs. Outer-Sphere Electron Transfer. The measured volume of activation ΔV_6^* for the electron transfer in reaction 6 is 13.0 cm³ mol⁻¹ more negative than ΔV_7^* for reaction 7.[16]

$$Fe(H_2O)_6^{2+} + Fe^*(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_6^{3+} + Fe^*(H_2O)_6^{2+} \quad (6)$$

$$Fe(H_2O)_6^{2+} + Fe^*(H_2O)_5OH^{2+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + Fe^*(H_2O)_6^{2+} \quad (7)$$

In either case ΔV^* may be regarded[16] as the sum of Coulombic, Debye–Hückel, solvent reorganization, and internal rearrangement terms, but of these only the first two are likely to be significantly different for pathways 6 and 7, since the sums of the effective hydrated-ion radii will be about the same[13] and the internal reorganization volume is always small.[16] Following Stranks,[16] but noting that all entries in the penultimate column of his Table 2[16] should be positive,[23] we calculate the Coulombic contribution to $\Delta\Delta V^*$ ($= \Delta V_6^* - \Delta V_7^*$) to be −2.4 cm³ mol⁻¹ and the Debye–Hückel component +1.3 cm³ mol⁻¹. Thus, if both paths are outer sphere, $\Delta\Delta V^*$ should be only about −1.1 cm³ mol⁻¹. Stranks[16] attributed the discrepancy to a change of mechanism to inner sphere in eq 7, the essential difference being the loss of a coordinated water molecule en route to the transition state in the latter.

Equation 1 enables us to calculate the limiting magnitude of this contribution to $\Delta\Delta V^*$ to be −13.4 ± 1.5 cm³ mol⁻¹ if the water molecule comes from the Fe(III) ion (Table I) or −13.1 ± 1.6 cm³ mol⁻¹ if, as is likely on grounds of lability, it comes from the Fe(II) (Figure 1). The calculated limiting value of $\Delta\Delta V^*$ is then −14.2 ± 1.6 cm³ mol⁻¹, which agrees sufficiently well with the observed value of −13.0 cm³ mol⁻¹ to suggest that the displaced water molecule in the inner-sphere mechanism is completely lost to bulk solvent in the activation process, i.e., that the lifetime of the presumed intermediate $(H_2O)_5Fe(OH)Fe(OH_2)_5^{4+}$ is at least comparable with the relaxation time of its solvation sheath. This conclusion is not adversely affected by the neglect of the small contraction expected from the conversion of $\{(H_2O)_5Fe\cdots HOFe(OH_2)_5\}^{4+}$ to $\{(H_2O)_5Fe\cdots(HO)\cdots Fe(OH_2)_5\}^{4+}$, as this would tend to make the calculated $\Delta\Delta V^*$ slightly less negative.

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Registry No. Na^+(aq), 40791-39-7; Mg^{2+}(aq), 19592-06-4; Al^{3+}(aq), 15453-67-5; Mn^{2+}(aq), 15365-82-9; Mn^{3+}(aq), 18976-26-6;

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Fe^{3+}(aq), 15377-81-8; Co^{2+}(aq), 15276-47-8; Ni^{2+}(aq), 15365-79-4; Cu^{2+}(aq), 14946-74-8; Zn^{2+}(aq), 15906-01-1; Ga^{3+}(aq), 19521-89-2; Y^{3+}(aq), 73890-49-0; Ag^{+}(aq), 42566-53-0; Cd^{2+}(aq), 14752-06-8; U^{4+}(aq), 86392-55-4.

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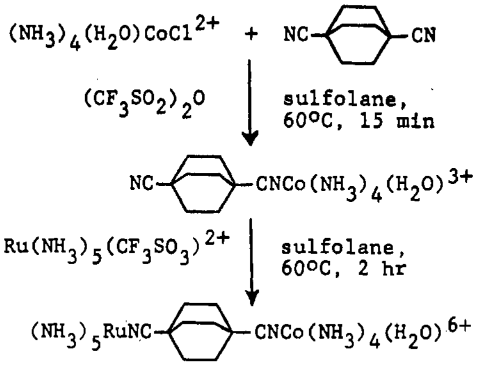
Inhibition of Thermal Electron Transfer by the Saturated Bridging Ligand in (μ-1,4-Dicyanobicyclo[2.2.2]octane)(pentaammineruthenium(II))aquotetraamminecobalt(III)

Sir:

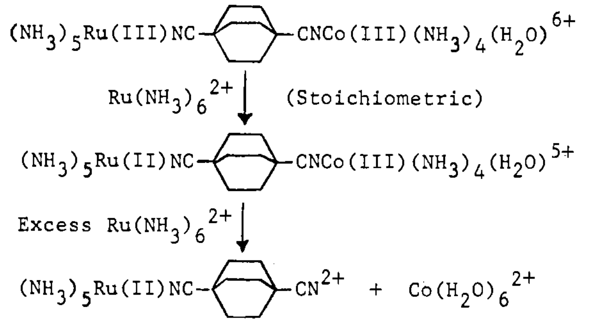
The reduction of oxygen to water in mitochondria involves a series of oxidation-reduction reactions that produce several ATP molecules for each oxygen atom that is reduced. The electron-transfer series involves metal-containing enzymes (cytochromes and ferredoxins) that do not react as they would be expected to react in homogeneous solution. Since many of these species are membrane bound, it has been widely assumed that the reaction specificity derives from the spatial arrangement of enzymes in and across mitochondrial membranes.[1] An important aspect of this arrangement is the distance that separates various components. Determining these distances in intact systems has been an intractable problem, and experimental results for protein complexes have also proven to be conjectural.[2] Some interesting data have recently been obtained in the laboratories of Gray and of Isied for individual proteins that have been chemically modified to include a redox center that can undergo an electron-transfer reaction with the native prosthetic group.[3,4] Comparison of results from structurally well-defined models and these protein complexes should be valuable in determining the types of mechanisms that may allow efficient electron-transfer reactions in natural systems. The aim of our work is to define parameters for rather simple, structurally well-defined complexes that contain reducing and oxidizing centers.

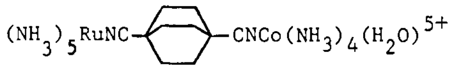
Several groups have been involved in developing systems to model the spatially separated metal-to-metal atom biological electron-transfer reactions. An appropriate system would involve electron transfer from one metal atom to another across a saturated bridge, which would separate the metal atoms by a known, fixed distance. In designing such systems, Taube and co-workers have ingeniously exploited two general patterns of metal ion reactivity: (1) the inertness to ligand exchange of metal atoms that have highly populated bonding and nonbonding orbitals and empty antibonding orbitals (low-spin d^5 and d^6 ions, Ru(III), Co(III) and Ru(II)) and (2) the sluggishness of reactions that involve a high Franck-Condon barrier (i.e. those of Co(III) → Co(II) relative to Ru(III) → Ru(II)).[5] Thus, a bimetallic complex with Co(III) and Ru(III) can remain intact in solution, and the addition of a suitable reducing agent will cause the Ru(III) atom to be reduced before the Co(III) atom even if the potential favors the Co(III) reduction. An additional advantage of this scheme is that subsequent reduction of the Co(III) site by the newly generated Ru(II) site produces $Co(H_2O)_6^{2+}$, which is very difficult to oxidize, rendering the reaction irreversible. Thus, even a reaction with an unfavorable free energy difference can be accomplished. In several reported applications of this scheme, a major difficulty has been encountered—saturated ligands are generally flexible and the first-order reactions that have been observed quite likely result from the reaction of the metal atom on one end of the bimetallic complex with the metal atom at the other end when the two metal atoms are in relatively close proximity. In this report, we present results for the first case of an unambiguously rigid, bimetallic complex that is capable of thermal electron transfer, (μ-1,4-dicyanobicyclo[2.2.2]octane)(pentaammineruthenium(II))aquotetraamminecobalt(III) (I).

Scheme I



Scheme II





I

This bimetallic complex is synthesized from $Co(NH_3)_4(H_2O)Cl^{2+}$, 1,4-dicyanobicyclo[2.2.2]octane, and $Ru(NH_3)_5(CF_3SO_3)^{2+}$ (Scheme I).[7] The visible-UV spectrum (498 nm, $\epsilon = 62$; 383 nm, shoulder; 283 nm, $\epsilon = 613$) is characteristic of $Co^{III}N_5O$ and $Ru^{III}(NH_3)_5NCR$ coordination spheres (where R is a bridgehead nitrile),[8] the cyclic voltam-

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