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Entropic Driving-Force Effects upon Preexponential Factors for Intramolecular Electron Transfer: Implications for the Assessment of Nonadiabaticity

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Considerable effort has been directed recently toward measuring rate parameters for intramolecular redox reactions, typically involving electron transfer between a pair of transition metals linked by an organic bridge.¹⁻³ Such reactions offer important advantages over bimolecular processes for investigating detailed aspects of electron transfer, since the uncertainties concerning the energetics of forming the precursor complex are absent and the geometry of the transition state is relatively well-defined.³

The study of intramolecular electron transfer should be particularly useful for examining electronic coupling effects; i.e. the factors influencing the occurrence and degree of nonadiabaticity.^{1b-d,3b,c,e} Since the rate constant, k_{et} , for such processes should refer to an elementary electron-transfer step, it can be expressed as⁴

$$k_{et} = \nu_n \kappa_{el} \exp(\Delta S_{FC}^*/R) \exp(-\Delta H_{FC}^*/RT) \quad (1a)$$

$$k_{et} = \nu_n \exp(\Delta S_a^*/R) \exp(-\Delta H_{FC}^*/RT) \quad (1b)$$

where ν_n is the effective nuclear frequency factor, κ_{el} is the electronic transmission coefficient, and ΔS_{FC}^* and ΔH_{FC}^* are the entropic and enthalpic components of the Franck-Condon barrier. Values of κ_{el} can therefore be extracted from rate measurements as a function of temperature provided that ν_n and ΔS_{FC}^* are known. For many reactions ν_n is numerically very similar to the conventional factor kT/h .⁵ Since work terms are absent for intramolecular reactions, the observation of preexponential factors that are substantially less than ν_n or, equivalently, of negative apparent entropies of activation ΔS_a^* (eq 1b) is often taken as prima facie evidence of nonadiabaticity (i.e. $\kappa_{el} < 1$). Implicit in this interpretation is the assumption that ΔS_{FC}^* is essentially zero. However, contrary to common belief, this is probably incorrect for most non-symmetrical intramolecular reactions, including those featuring charge symmetry. The purpose of this note is to explore the likely magnitudes of ΔS^* for some representative intramolecular reactions and to examine the consequences for the interpretation of unimolecular preexponential factors in terms of nonadiabaticity.

The origin of the Franck-Condon activation entropy can be clarified by considering Marcus' expression⁶ for the activation free energy, ΔG_{FC}^* , and its temperature derivative. Thus⁷

$$\Delta G_{FC}^* = \Delta G_{int}^* + 0.5(1 + \alpha)\Delta G^\circ \quad (2)$$

where ΔG_{int}^* is the intrinsic barrier, ΔG° is the thermodynamic free energy change, and $\alpha = \Delta G^\circ/8\Delta G_{int}^*$. The temperature derivative of eq 2 is

$$\Delta S_{FC}^* = \Delta S_{int}^*(1 - 4\alpha^2) + 0.5(1 + 2\alpha)\Delta S^\circ \quad (3)$$

where ΔS_{int}^* is the intrinsic activation entropy and ΔS° is the entropic driving force. For reactions having small or moderate values of ΔG° , $\alpha = 0$ so that eq 3 simplifies to

$$\Delta S_{FC}^* \approx \Delta S_{int}^* + 0.5\Delta S^\circ \quad (3a)$$

For reactions in aqueous media, ΔS_{int}^* is usually assumed to be close to zero (within ca. 0.5 eu) as predicted by the conventional dielectric continuum expression,⁸ although there is good reason to suspect that small positive values of ΔS_{int}^* (ca. 1-3 eu) are common.⁹ However, ΔS° can often be sufficiently large to yield a substantial contribution to ΔS_{FC}^* , even for reactions leading to no net change in ionic charge. For example, the reduction of $\text{Fe}(\text{phen})_3^{3+}$ (phen = phenanthroline) by $\text{Fe}(\text{OH}_2)_6^{2+}$ yields a net entropy change of -40 eu,¹² corresponding to a value of ΔS_{FC}^* of ca. -16 eu from eq 3.

The values of ΔS° can be related to the component entropic changes (the so-called "reaction entropies" ΔS_{rc}° ¹⁰) at the redox centers undergoing reduction and oxidation, $\Delta S_{rc,red}^\circ$ and $\Delta S_{rc,ox}^\circ$, respectively, by

$$\Delta S^\circ = \Delta S_{rc,red}^\circ - \Delta S_{rc,ox}^\circ \quad (4)$$

Such large entropic driving forces arise because the component reaction entropies are often large and extremely sensitive not only to the charge type of the redox couple but also to the chemical nature of the coordinated ligands, the metal redox center, and the surrounding solvent.^{10,13,14} This is due to the large changes in the extent of local solvent polarization brought about by electron transfer.^{10,14,15}

In order to check the validity of eq 3, values of ΔS_{FC}^* were calculated for 30 outer-sphere bimolecular reactions and compared with the experimental activation entropies, ΔS_{expt}^* . The choice of reactions was limited to those for which values of ΔS° and ΔG° are available and sufficient structural information exists to permit the calculation of ΔG_{int}^* . Details will be presented elsewhere.¹⁶ All these reactions involve reactant pairs having charges of 3+ and 2+. Figure 1 is the resulting plot of ΔS_{expt}^* against ΔS_{FC}^* .¹⁷ This plot demonstrates that the experimental activation entropies do indeed

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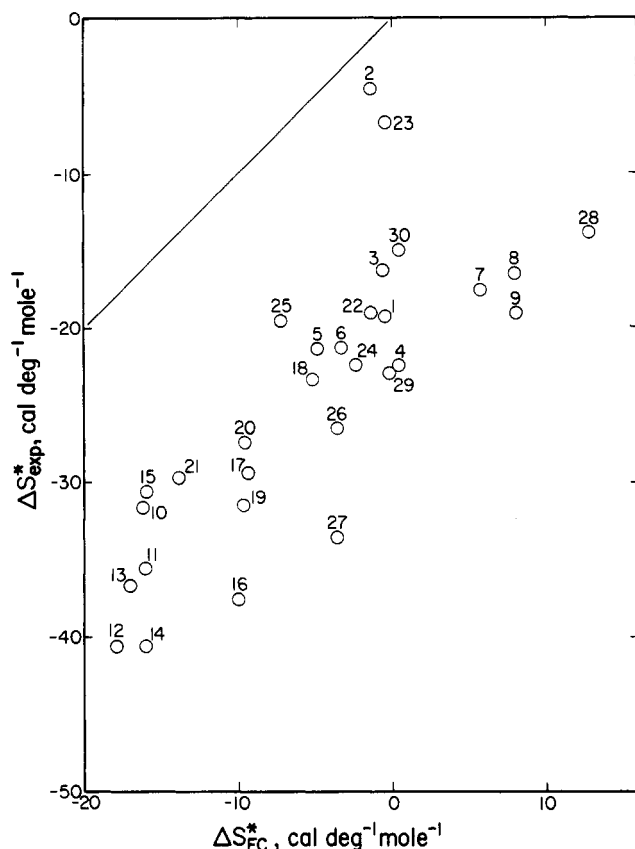


Figure 1. Plot of the experimental activation entropy,¹⁷ $\Delta S_{\text{exp}}^{\ddagger}$, against the activation entropy, $\Delta S_{\text{FC}}^{\ddagger}$, calculated from eq 3 for bimolecular reactions involving $3+/2+$ redox couples. Data sources are quoted in ref 18 unless otherwise noted (aq = OH_2 , en = ethylenediamine, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, terpy = 2,2',2''-terpyridine, py = pyridine). Reactions: 1, $\text{Co}_{\text{aq}}^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 2, $\text{Co}_{\text{aq}}^{3+} + \text{Cr}_{\text{aq}}^{3+}$; 3, $\text{Fe}_{\text{aq}}^{3+} + \text{Ru}_{\text{aq}}^{2+}$; 4, $\text{Fe}_{\text{aq}}^{3+} + \text{V}_{\text{aq}}^{2+}$; 5, $\text{Fe}_{\text{aq}}^{3+} + \text{V}_{\text{aq}}^{2+}$; 6, $\text{V}_{\text{aq}}^{3+} + \text{V}_{\text{aq}}^{2+}$; 7, $\text{Fe}_{\text{aq}}^{3+} + \text{Ru}(\text{NH}_3)_6^{2+}$; 8, $\text{Fe}_{\text{aq}}^{3+} + \text{Ru}(\text{NH}_3)_5\text{py}^{2+}$; 9, $\text{Fe}_{\text{aq}}^{3+} + \text{Ru}(\text{en})_3^{2+}$; 10, $\text{Ru}(\text{bpy})_3^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 11, $\text{Ru}(\text{phen})_3^{3+} + \text{Ru}_{\text{aq}}^{2+}$; 12, $\text{Fe}(\text{bpy})_3^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 13, $\text{Fe}(\text{phen})_3^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 14, $\text{Ru}(\text{terpy})_2^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 15, $\text{Ru}(\text{bpy})_2(\text{py})_2^{3+} + \text{Fe}_{\text{aq}}^{2+}$; 16, $\text{Ru}(\text{NH}_3)_6^{3+} + \text{V}_{\text{aq}}^{2+}$; 17, $\text{Ru}(\text{NH}_3)_5\text{py}^{3+} + \text{V}_{\text{aq}}^{2+}$; 18, $\text{Co}(\text{en})_3^{3+} + \text{V}_{\text{aq}}^{2+}$; 19, $\text{Co}(\text{bpy})_3^{3+} + \text{V}_{\text{aq}}^{2+}$; 20, $\text{Co}(\text{phen})_3^{3+} + \text{V}_{\text{aq}}^{2+}$; 21, $\text{Ru}(\text{NH}_3)_5\text{py}^{3+} + \text{Cr}_{\text{aq}}^{3+}$; 22, $\text{Ru}(\text{NH}_3)_4\text{bpy}^{3+} + \text{Ru}(\text{NH}_3)_4\text{phen}^{2+}$; 23, $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Ru}(\text{NH}_3)_6^{2+}$; 24, $\text{Ru}(\text{en})_3^{3+} + \text{Ru}(\text{NH}_3)_6^{2+}$; 25, $\text{Co}(\text{en})_3^{3+} + \text{Co}(\text{en})_3^{2+}$; 26, $\text{Co}(\text{bpy})_3^{3+} + \text{Co}(\text{bpy})_3^{2+}$; 27, $\text{Co}(\text{phen})_3^{3+} + \text{Co}(\text{phen})_3^{2+}$; 28, $\text{Co}(\text{en})_3^{3+} + \text{Cr}(\text{bpy})_3^{2+}$; 29, $\text{Co}(\text{phen})_3^{3+} + \text{Ru}(\text{NH}_3)_6^{2+}$; 30, $\text{Co}(\text{phen})_3^{3+} + \text{Ru}(\text{NH}_3)_5\text{py}^{2+}$.

respond to the entropic driving force roughly in the manner predicted by eq 3, although the values of $\Delta S_{\text{exp}}^{\ddagger}$ are about 15–25 eu smaller than $\Delta S_{\text{FC}}^{\ddagger}$. (Also note that reactions involving high-spin Co(III)/Co(II) couples do not display noticeably different behavior in spite of the spin state change that occurs for these reactions.) This discrepancy could be taken as an indication of nonadiabaticity ($\kappa_{\text{el}} \ll 1$), but more likely it arises chiefly from an additional component of $\Delta S_{\text{exp}}^{\ddagger}$ associated with the unfavorable entropic work of forming the highly charged precursor complex from the separated cationic reactants.^{3b,11,18}

Most nonsymmetrical intramolecular reactions will also have nonzero entropic driving forces, thereby yielding nonzero values of $\Delta S_{\text{FC}}^{\ddagger}$ on the basis of eq 3. This is most obviously the case for systems where electron transfer leads to a net charge decrease at the redox centers, such as the pentaamminecobalt(III)–pentacyanoiron(II) reactions examined by Haim and co-workers.² Here the values of $\Delta S_{\text{rc,red}}^{\circ}$ and $\Delta S_{\text{rc,ox}}^{\circ}$ will be positive and negative, respectively (Table I), yielding large

Table I. Reaction Entropies, $\Delta S_{\text{rc}}^{\circ}$ (cal deg⁻¹ mol⁻¹) for Various Redox Couples in Aqueous Solution^a

redox couple ^b	metal center		
	Co	Ru	Fe
$\text{M}(\text{2-bpy})_3^{3+/2+}$	22	1	2
$\text{M}(\text{phen})_3^{3+/2+}$	22		3
$\text{M}(\text{OH}_2)_6^{3+/2+}$	~60 ^c	36	43
$\text{M}(\text{en})_3^{3+/2+}$	37	13	
$\text{M}(\text{NH}_3)_6^{3+/2+}$	~45 ^d	18	
$\text{M}(\text{NH}_3)_5(\text{bpy})^{3+/2+}$		15 ^e	
$\text{M}(\text{NH}_3)_5\text{py}^{3+/2+}$		17	
$\text{M}(\text{NH}_3)_5\text{OH}^{3+/2+}$		25	
$\text{M}(\text{NH}_3)_5\text{NCS}^{2+/+}$		15	
$\text{M}(\text{NH}_3)_5\text{Cl}^{2+/+}$		10	
<i>cis</i> - $\text{M}(\text{NH}_3)_4\text{Cl}_2^{2+/+}$		10	
$\text{M}(\text{CN})_6^{3-/4-}$			-42, ^f -23 ^{e,g}
$\text{M}(\text{CN})_4\text{bpy}^{-1/2-}$			-29 ^f

^a Ionic strength $\mu \sim 0.1$; data taken from ref 10 and 13, except where noted. ^b M denotes metal redox centers. Ligand abbreviations: 2-bpy = 2,2'-bipyridine; bpy = 4,4'-bipyridine; phen = 1,10-phenanthroline; en = ethylenediamine; py = pyridine. ^c Estimated from thermodynamic data corrected for temperature dependence of reference electrode and likely ionic strength effects; data from: Noyes, A. A.; Deahl, T. J. *J. Am. Chem. Soc.* **1937**, *59*, 1337. A similar value (ca. ± 5 eu) is obtained from a correlation of $\Delta S_{\text{rc}}^{\circ}$ with the self-exchange rate constant k_{ex} ,²⁰ on the assumption that $k_{\text{ex}} \sim 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$.²¹ ^d Estimated by comparison with corresponding value for $\text{Co}(\text{en})_3^{3+/2+}$. ^e Hupp, J. T., unpublished experiments. ^f Ionic strength $\mu \rightarrow 0$. ^g Determined in 0.2 M $\text{La}(\text{ClO}_4)_3$.

positive values of ΔS° (eq 4) and, hence, $\Delta S_{\text{FC}}^{\ddagger}$ (eq 3), due to the decrease in solvent polarization attending such charge neutralization.^{2c} Quantitative values of ΔS° for these systems are difficult to estimate from values of $\Delta S_{\text{rc}}^{\circ}$ for the isolated redox centers. This is because $\Delta S_{\text{rc}}^{\circ}$ for cyano Fe(III)/Fe(II) couples is known to be extremely sensitive to the cationic environment (Table I)¹⁹ so that the proximity of the cationic Co(III)/Co(II) redox center is expected to influence the solvation around Fe(III)/Fe(II) . Nevertheless, from the $\Delta S_{\text{rc}}^{\circ}$ values in Table I, we estimate that $\Delta S_{\text{rc}}^{\circ}$ equals roughly 30 eu and -10 eu for the $[\text{Co}(\text{NH}_3)_5\text{L}]^{3+/2+}$ and $[\text{LFe}(\text{CN})_5]^{2-/3-}$ fragments, where L is a pyridine-type ligand, yielding $\Delta S^{\circ} \sim 40$ eu (eq 4) and $\Delta S_{\text{FC}}^{\ddagger} \sim 20$ eu (eq 3a). Indeed, values of ΔS_a^{\ddagger} of this order are obtained for $(\text{CN})_5\text{Fe}^{\text{II}}\text{--L--Co}^{\text{III}}(\text{NH}_3)_5$ reactions.^{2d} Similarly, large values of ΔS° are expected for the intramolecular reduction of pentaamminecobalt(III) by the *p*-nitrobenzoate radical anion since both redox centers will again contribute positive components to ΔS° , thereby explaining the large preexponential factors (i.e. positive values of ΔS_a^{\ddagger}) observed for these reactions.²⁹

Substantial values of ΔS° are expected also for intramolecular reactions between pairs of metal redox centers having the same charge type and similar ligand environments but with different electronic configurations. Important examples of this type are the pentaamminecobalt(III)–aquotetraammine-ruthenium(II) reactions bridged by nitrogen heterocyclic lig-

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ands that have been studied by Taube and co-workers.¹ Since these reactions are charge symmetric, it is usually tacitly assumed that $\Delta S^\circ \approx 0$ and hence $\Delta S_{FC}^* \approx 0$.^{1b,3b,c} However, since reaction entropies for high-spin Co(III)/Co(II) couples are generally found to be markedly larger than for Ru(III)/Ru(II) and other low-spin couples (Table I),^{10,13} large positive values of ΔS° and hence ΔS_{FC}^* are therefore anticipated for these reactions.

As an illustrative example, we consider the intramolecular reduction of Co(III) by Ru(II) in $(H_2O)Ru(NH_3)_4(bpy)Co(NH_3)_5^{5+}$ (where bpy = 4,4'-bipyridine). The reaction for the corresponding decaammine complex $Ru(NH_3)_5(bpy)Co(NH_3)_5^{5+}$ is liable to involve a net entropy change of ca. 20–25 eu since the reaction entropies of Co(III)/Co(II) and Ru(III)/Ru(II) couples having similar ligands uniformly differ by this amount (Table I).^{10,14} The effect of replacing one ammonia on ruthenium by an aquo ligand can be gauged from the 7 eu larger reaction entropy for $Ru(NH_3)_5OH_2^{3+/2+}$ than for $Ru(NH_3)_6^{3+/2+}$ (Table I). (To a first approximation, the reaction entropies for mixed-ligand complexes appear to arise from linear additive contributions from each ligand.¹³) Thus, the entropic driving force for electron transfer in $(H_2O)Ru^{II}(NH_3)_4(bpy)-Co^{III}(NH_3)_5^{5+}$ is estimated to be ca. +15 eu. Bearing in mind the likely value of ΔS_{int}^* (1–2 eu⁹), a value of ΔS_{FC}^* of ca. 8 eu is obtained from eq 3a. Therefore, the "measured" activation entropy, ΔS_a^* , of 2.5 eu for this system is suggestive of a significantly nonadiabatic pathway ($\kappa_{el} \sim 0.1$ (eq 1)) rather than the adiabatic pathway that has been inferred without consideration of the entropic driving force.^{1b,c} Since similar values of ΔS_{FC}^* should also be appropriate for other $(H_2O)Ru^{II}(NH_3)_4LCo^{III}(NH_3)_5^{5+}$ reactions with related bridging ligands L, the smaller or negative values of ΔS_a^* seen, for instance, with L = 1,2-bis(4-pyridyl)ethylene (1.3 eu) and 1,2-bis(4-pyridyl)ethane (–9.6 eu)^{3b,c} infer the presence of decidedly nonadiabatic pathways. Thus, from eq 1, if $\Delta S_{FC}^* = 8$ eu, then κ_{el} is $\sim 3 \times 10^{-2}$ and $\sim 1 \times 10^{-4}$ for these two reactions, respectively.

Naturally, these resulting κ_{el} values should be regarded as being only approximate. Since the values of ΔS_{rc}° for the intramolecular binuclear reactions are inferred from data for structurally similar mononuclear couples, the reliability of the resulting estimates of ΔS° and hence ΔS_{FC}^* may be called into question. Unfortunately, values of ΔS° cannot be measured directly for these and other thermal intramolecular reactions on account of the rapid aquation that follows the formation of Co(II). However, Steggerda et al. have shown that the values of ΔS_{rc}° for mononuclear Ru(III)/Ru(II) couples containing pyrazine ligands are essentially the same as in binuclear complexes where the pyrazine ligand is also bound to another ruthenium redox center.³⁰ This result therefore provides strong support to the present method for estimating ΔS° values for binuclear complexes. Providing that the present estimates of ΔS° are accurate to within ca. 5 eu, which seems reasonable, then the corresponding estimates of κ_{el} are reliable within ca. 4-fold.

Such entropic driving-force effects also provide a rationalization of the substantially more positive value of ΔS_a^* , 10.4 eu, for electron transfer in $(SO_3)Ru^{II}(NH_3)_4(pyr)Co^{III}(NH_3)_5^{5+}$,^{1d} especially in comparison with that for $(H_2O)Ru^{II}(NH_3)_4(bpy)Co^{III}(NH_3)_5^{5+}$, 2.6 eu. This increase is difficult to explain on the basis of electronic coupling effects^{1d}

but can easily be understood in terms of the influence of nonbridging ligand composition on ΔS° and hence ΔS_{FC}^* . The presence of anionic ligands generally yields substantially smaller values of ΔS_{rc}° .^{10,13} The influence of substituting an aquo for a sulfite ligand on the reaction entropy of Ru(III)/Ru(II) can be gauged roughly from the decrease in ΔS_{rc}° 15 eu, between $Ru(NH_3)_5OH_2^{3+/2+}$ and $cis-Ru(NH_3)_4Cl_2^{7/0}$ (Table I),¹⁰ corresponding to an increase in ΔS_{FC}^* of ca. 8 eu (Eq 3a) since the ruthenium undergoes oxidation.

Similar considerations can also be applied to a number of other intramolecular reactions, such as those involving non-symmetrical bridging ligands.^{1d,32} We have also recently analyzed activation parameter data for a number of intramolecular redox reactions at metal surfaces (i.e. electrochemical processes involving adsorbed reactants) in a similar manner.³³ Entropic driving-force effects are generally important for these processes since only one redox center is involved, so that ΔS° equals ΔS_{rc}° . The estimation of ΔS_{FC}^* for intramolecular systems should be approached with caution since the factors influencing the thermodynamic entropy changes are incompletely understood. Nevertheless, it is clear that careful consideration of the ligand composition and the chemical as well as electrostatic nature of the redox centers is required in order to evaluate the contribution of the Franck-Condon entropy to the measured preexponential factors.

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Unexpected Formation of *cis*- and *trans*- $Ph_2PCH=CHPPh_2$ by Reaction of Lithiobis(diphenylphosphino)methane and Dichloromethane. ¹³C NMR Studies of the Products

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Lithiobis(diphenylphosphino)methane (**1**) shows an ambivalent reactivity toward organo halides.^{1,2} The carbanionic center as well as the two trivalent phosphorus atoms may be attacked alternatively by the electrophiles RX. Reactions of **1** with methyl iodide or benzyl chloride proceed according to (1) while diphenylchlorophosphine affords products of type **3**. If instead of **1** the methylated derivative $[Li(TMED)]^+ [Ph_2PCHPPhMe]^-$ (TMED = tetramethylethylenediamine) is used, dialkylchlorophosphines R'_2PCl ($R' = t-C_4H_9$, C_6H_{11}) attack at the more basic phosphorus atom, forming products of type **3**, $Ph_2PCH=PPhMePR'_2$.²

Looking for synthetic routes to new polydentate phosphine ligands with P–C–P units, we studied the reaction between **1**

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