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Communications

Concerning the Nonadiabaticity Problem in Outer-Sphere Electron- and Energy-Transfer Reactions

Sir:

In the last three decades there has been considerable interest in the experimental and theoretical aspects of electron-transfer reactions.[1-11] While much progress has been made toward a better understanding of this fundamental class of chemical reactions, there is still a strong debate on the role played by electronic factors in determining the rate constants (nonadiabaticity problem).[3,4,6-8,10-12] In the meantime, it has been shown that the formalism used for outer-sphere electron-transfer reactions can profitably be extended to the discussion of energy-transfer processes.[13-17]

In recent years we have used an approach[7,18-20] based on free energy correlation of rate constants[21] that in favorable cases can contribute to elucidate problems concerning nuclear factors in electron-[22] and energy-transfer[13,15,17,23] processes. In particular, this approach has shown that in some electron-[18,24-26] and energy-transfer[13b,14,16,17,23b,27,28] processes the electronic transmission coefficient is lower than unity (nonadiabatic behavior). In a communication in this journal Furholz and Haim (FH)[29] have criticized our approach and have presented an "alternate" approach to the nonadiabaticity problem. We would like to consider briefly their criticisms and to discuss in some detail the relationship between our approach and their "alternate" one, with particular emphasis on the use of the two approaches for comparative and predictive purposes.

Both FH's and our approaches are based on free energy correlation of rate constants. Approaches of this type are open to criticisms, and the status of the electron-transfer theory itself is perhaps not fully satisfactory. However, while we are waiting for slowly appearing, more direct experimental approaches,[30] the use of relations between rates of self-exchange and electron-transfer cross-reactions continues to be an important means to obtain mechanistic information on bimolecular reactions in fluid solutions. The cases of breakdown of the Marcus cross-relation[2] can be particularly interesting, as earlier noticed by Sutin and coworkers.[31]

Approach to Electron-Transfer Kinetics. As discussed in more detail elsewhere,[7,18,21] application of the steady-state approximation to the sequence of elementary steps in eq 1 yields eq 2, where k_{AB}

$$\mathrm{A} + \mathrm{B} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \mathrm{A{\cdot}B} \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \mathrm{A^-{\cdot}B^+} \underset{k'_d}{\overset{k'_{-d}}{\rightleftharpoons}} \mathrm{A^-} + \mathrm{B^+} \qquad (1)$$

$$k_{AB} = k_d \Big/ \left(1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}k_{-e}}{k'_{-d}k_e} \right) \qquad (2)$$

is the second-order rate constant for the electron-transfer reaction between A and B, k_d, k'_d, k_{-d}, and k'_{-d} are rate constants for formation and dissociation of the outer-sphere encounter complex, and k_e and k_{-e} are unimolecular rate constants for electron transfer. If a classical approach is used,[7,10] k_{-e}/k_e is given by $\exp(\Delta G_{AB}/RT)$, where ΔG_{AB} is the free energy change of the elec-

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(1) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
(2) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
(3) Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; *Tunneling in Biological Systems*; Academic: New York, 1979.
(4) Ulstrup, J. *Charge Transfer Processes in Consensed Media*; Springer-Verlag: West Berlin, 1979.
(5) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.
(6) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225; **1982**, *15*, 275.
(7) Balzani, V.; Scandola, F. In *Energy Resources through Photochemistry and Catalysis*; Graetzel, M., Ed.; Academic: New York, 1983.
(8) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. *Prog. Inorg. Chem.* **1983**, *30*, 141.
(9) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389.
(10) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(11) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.
(12) Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127.
(13) Balzani, V.; Bolletta, F. *J. Am. Chem. Soc.* **1978**, *100*, 7404. Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.
(14) Balzani, V.; Indelli, M.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852.
(15) Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. *Chem. Phys.* **1980**, *52*, 313.
(16) Endicott, J. F.; Heeg, M. J.; Gaswick, D.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777.
(17) Scandola, F.; Balzani, V. *J. Chem. Educ.* **1983**, *60*, 814.
(18) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.
(19) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.
(20) Balzani, V.; Scandola, F. In *Photochemical Conversion and Storage of Solar Energy*; Connolly, J. S., Ed.; Academic: New York, 1981.
(21) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259.
(22) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.
(23) (a) Wirz, J.; Krebs, A.; Schmalstieg, H.; Angliker, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 192. (b) Wilkinson, F.; Tsiamis, C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1681.
(24) Sabbatini, N.; Indelli, M.T.; Gandolfi, M. T.; Balzani, V. *J. Phys. Chem.* **1982**, *86*, 3585.
(25) Sandrini, D.; Gandolfi, M. T.; Maestri, M.; Bolletta, F.; Balzani, V. *Inorg. Chem.* **1984**, *23*, 3017.
(26) Sandrini, D.; Maestri, M.; Belser, P.; von Zelewsky, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3675.
(27) Wilkinson, F.; Tsiamis, C. *J. Phys. Chem.* **1981**, *85*, 4153.
(28) Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435.
(29) Furholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 3091.
(30) See, for example: (a) Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442. (b) Rybak, W.; Haim, A.; Netzel, T. J.; Sutin, N. *J. Phys. Chem.* **1981**, *85*, 2856. (c) Reagor, B. T.; Kelley, D. F., Huchital, D. H.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 7400. (d) Ballardini, R.; Gandolfi, M. T., Balzani, V. *Chem. Phys. Lett.* **1985**, *119*, 459. (e) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. (f) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571. (g) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.
(31) Campion, R. J.; Purdie, N.; Sutin, N. *Inorg. Chem.* **1964**, *3*, 1091.

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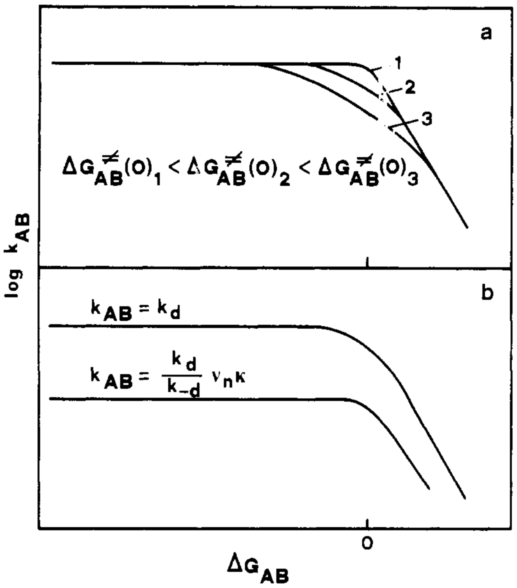

Figure 1. Effects of nuclear barriers (a) and nonadiabaticity (b) on log k_{AB} vs. ΔG_{AB} plots. For more details, see text and ref 7 and 20.

tron-transfer step, and the rate constant of electron transfer is given by eq 3, where κ_{AB} is the electronic transmission coefficient,

$$k_e = \kappa_{AB}\nu_n \exp(-\Delta G^{\ddagger}_{AB}/RT) \qquad (3)$$

ν_n is an effective frequency for nuclear motion, and $\Delta G^{\ddagger}_{AB}$ is the free activation energy, which may be expressed by the free-energy relationship[32]

$$\Delta G^{\ddagger}_{AB} = \Delta G_{AB} + \frac{\Delta G^{\ddagger}_{AB}(0)}{\ln 2}\left[1 + \exp\left(-\frac{\Delta G_{AB}(\ln 2)}{\Delta G^{\ddagger}_{AB}(0)}\right)\right] \qquad (4)$$

where $\Delta G^{\ddagger}_{AB}(0)$ is the so-called intrinsic nuclear barrier. For a homogeneous series of reactions,[7,19,20] such as those between the same reductant A and a series of structurally related oxidants B_1, B_2, B_3, ..., which have variable redox potential but the same size, shape, electronic structure, and electric charge, one can assume that throughout the series the reaction parameters k_d, k_{-d}, and k'_{-d} in eq 2, κ_{AB} and ν_n in eq 3, and $\Delta G^{\ddagger}_{AB}(0)$ in eq 4 are constant. Under these assumptions, k_{AB} (eq 2) is only a function of ΔG_{AB}, and when the values of the other parameters are known, a two-parameter fit of the log k_{AB} vs. ΔG_{AB} plot to eq 2–4 may allow, in principle, an estimate of the values of $\Delta G^{\ddagger}_{AB}(0)$ and κ_{AB} of the homogeneous series of reactions. When either $\Delta G^{\ddagger}_{AB}(0)$ or κ_{AB} is known from other experimental results (or can be estimated from reasonable assumptions), a more reliable one-parameter fit can be used to estimate the unknown quantity. Aside from these quantitative implications, the model has a qualitative predictive value.[7,17,19,20] In particular, large nuclear barriers are expected to reveal themselves from the nonlinear intermediate region of the plot (Figure 1a), while nonadiabaticity is expected to cause a rate saturation below the diffusion-controlled limit at high driving force (Figure 1b).

The model has been further elaborated[7,19,20,25,26] in an attempt to obtain parameters related to the individual reactants. To do that, the relationships

$$\Delta G^{\ddagger}_{AB}(0) = \frac{\Delta G^{\ddagger}_{AA} + \Delta G^{\ddagger}_{BB}}{2} \qquad (5)$$

$$\kappa_{AB} = (\kappa_{AA}\kappa_{BB})^{1/2} \qquad (6)$$

were used. Equation 5 is the well-known relation of the Marcus adiabatic theory, which links the rates of a cross-reaction to the rates of the corresponding self-exchange reactions,[10,33] and eq 6, first proposed by Sutin,[6] expresses the condition that would allow the Marcus adiabatic cross-relation to be obeyed by not too exergonic nonadiabatic reactions.[10] Equation 6 is not expected to have general applicability,[6,10] but it still represents a useful tool to compare and discuss experimental results.[34,35]

Furholz and Haim's Specific Criticisms. FH[29] make note of the fact that our approach has a limited sensitivity to κ in the mildly nonadiabatic regime ($\kappa \geqslant 10^{-3}$). This limitation is repeatedly stated and discussed in our papers[36] and, being intrinsic to such free energy correlations, is also present in the "alternate" FH[29] approach. Of course, the actual sensitivity depends on the quality of the data that are to be fit. To emphasize their criticism, FH[29] focus their attention of the $Fe^{3+/2+}$ couple. This, however, is an odd choice because we did not use this couple to test our nonadiabaticity approach.[19] Rather, we assumed that the electronic transmission coefficient of this couple was within the limits 1 to 1 × 10^{-3} (nearly adiabatic behavior) to obtain an estimate of $\Delta G^{\ddagger}_{Fe^{3+}/Fe^{2+}}$, in the same way as we assumed a unitary transmission coefficient for the $Ru(NH_3)_6^{3+/2+}$ couple to evalaute its self-exchange barrier. The behavior in a series of homogeneous cross-reactions of these two substantially adiabatic couples, one having a large and the other a small intrinsic barrier, was then contrasted with that of the Eu^{3+}/Eu^{2+} couple, which was shown to exhibit a strongly nonadiabatic character (κ estimated to be $\leqslant 10^{-10}$).[19] The specific value assumed for $\kappa_{Fe^{3+}/Fe^{2+}}$ (within the 1 to 1 × 10^{-3} limits) was irrelevant for the purposes of our paper; therefore, our misinterpretation of a previously reported electronic factor, which led us to choose the value 2.5 × 10^{-3} for $\kappa_{Fe^{3+}/Fe^{2+}}$, was of little consequence in the context used. However, FH[29] are correct in noting that, in the case of the Fe^{3+}/Fe^{2+} data, the fits are rather insensitive to κ.

The specific objections raised by FH[29] on our Co(III) paper[25] only concern the homogeneization procedure.[37] In this context, we would like to point out the following: (i) Homogenization for the energy barrier of the reaction partner ($\Delta G^{\ddagger}_{BB}$) only implies the knowledge of (or a reasonable assumption on) either $\Delta G^{\ddagger}_{AA}$ *or* κ_{AA}; therefore, there are no elements of circular reasoning when the parameter to be obtained from the best fitting of the homogenized data is the one *not* used in the homogenization procedure. (ii) It can be easily shown that the k_{AB} values corrected for a different energy barrier are quite insensitive (over the whole ΔG range) to the order of magnitude (at least from 1 to 10^{-5}) of the κ_{AA} value used for the homogenization; thus, in the Co(III) paper the best fitting curve was first obtained by excluding the few cases in which the partner had a different intrinsic barrier variation, and then homogenization for intrinsic barrier was carried out by using the κ_{AA} value obtained from the first fitting. The homogenized data so obtained were found to lie practically on the best fitting curve. Thus, no iterative procedure was needed.

As first pointed out by Sutin and co-workers,[31] the rate constant for a self-exchange reaction derived from a cross-reaction may be different from the experimentally measured self-exchange rate constant. This breakdown of the cross-relation can yield mechanistic information,[31] as also noted by us[19,38] and by FH.[29] The

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(32) This equation was first derived by Marcus (*J. Phys. Chem.* **1968**, *72*, 891) for atom- and proton-transfer reactions and then used by Agmon and Levine (*Chem. Phys. Lett.* **1977**, *52*, 197) to discuss concerted reaction kinetics. In our approach eq 4 is used in a purely empirical way.

(33) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(34) The condition expressed by eq 6 (i.e. that the interaction energy in the cross-reaction is approximately equal to the geometric mean of the interaction energies in the corresponding exchange reactions) is theoretically reasonable when the contact between the reactants in both the cross-reaction and the exchange reaction occurs through identical or related atoms.[35]

(35) German, E. D. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1153.

(36) See, e.g., ref 17, p 820, for energy-transfer processes and ref 20, p 115, for electron-transfer processes.

(37) FH[29] also say that the situation in our Co(III) paper[25] is unsatisfactory "because there are few available reactions with homogeneous reagents" discussed. We would like to point out that the "few available reactions" were 11 for $Co(NH_3)_6^{3+}$ (and $Co(NH_3)_5(H_2O)^{3+}$), four for $Co(en)_3^{3+}$, and six for $Co(bpy)_3^{3+}$ (and $Co(phen)_3^{3+}$).

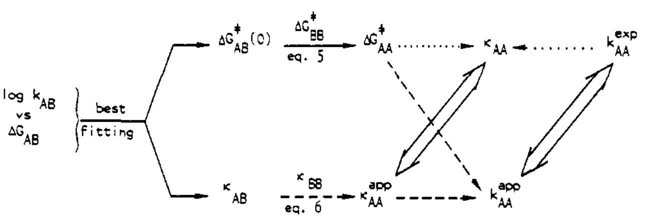
(38) Sabbatini, N.; Dellonte, S.; Bonazzi, A.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 1738.

Table I. Parameters for the Self-Exchange Reactions and Cross-Reactions of Co(III) Complexes

	$\Delta G^{\ddagger}{}_{AB}(0)$,[a] kcal mol^{-1}	κ_{AB}[a]	$\Delta G^{\ddagger}{}_{AA}$,[b] kcal mol^{-1}	$\kappa_{AA}{}^{app}$[c]	κ_{AA}[d]	$k_{AA}{}^{app}$,[e] M^{-1} s^{-1}	$k_{AA}{}^{exptl}$,[f] M^{-1} s^{-1}
$Co(NH_3)_6{}^{3+/2+}$[g]	15	3×10^{-1}	24	1×10^{-1}	3×10^{-1}	2×10^{-6}	8×10^{-6}[h]
$Co(en)_3{}^{3+/2+}$	11.5	3×10^{-2}	17	1×10^{-3}	8×10^{-5}	9×10^{-4}	8×10^{-5}[i]
$Co(bpy)_3{}^{3+/2+}$[j]	9.5	3×10^{-3}	13	1×10^{-5}	5×10^{-3}	3×10^{-2}	2×10^{1}

[a] Data obtained in ref 25 from the best fitting of the log k_{AB} vs. ΔG_{AB} plots of the cross-reactions with Ru– and Os–polypyridine complexes. [b] Obtained from $\Delta G^{\ddagger}{}_{AB}(0)$, $\Delta G^{\ddagger}{}_{BB}$, and eq 5 (ref 25). [c] Obtained from κ_{AB}, κ_{BB}, and eq 6 (ref 25). [d] Obtained from $k_{AA}{}^{exptl}$ and $\Delta G^{\ddagger}{}_{AA}$ by using the equation $k_{AA}{}^{exptl} = (k_d/k_{-d})\kappa_{AA}(kT/h) \exp(-\Delta G^{\ddagger}{}_{AA}/RT)$. [e] Obtained from $\kappa_{AA}{}^{app}$ and $\Delta G^{\ddagger}{}_{AA}$ by using the equation $k_{AA}{}^{app} = (k_d/k_{-d})\kappa_{AA}{}^{app}(kT/h) \exp(-\Delta G^{\ddagger}{}_{AA}/RT)$. [f] Experimental values of the self-exchange rate constants. [g] The cross-reactions used to obtain the data actually involved either $Co(NH_3)_6{}^{3+/2+}$ or $Co(NH_3)_5(H_2O)^{3+/2+}$ (ref 25). [h] From: Hammershøi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979. [i] From ref 10. [j] The cross-reactions used to obtain the data actually involved either $Co(bpy)_3{}^{3+/2+}$ or $Co(phen)_3{}^{3+/2+}$.

Scheme I



comparison between "apparent" (i.e. derived from cross-reactions) and experimental self-exchange rate constants is discussed in the following paragraph.

Comparison of the Two Approaches. The approach proposed by FH[29] is the same as that previously proposed by us,[7,19,20,25,26] except for the following points:

(a) Instead of the free-energy relationship expressed by eq 4, FH[29] use the classical Marcus quadratic relationship:[33]

$$\Delta G^{\ddagger}{}_{AB} = \Delta G^{\ddagger}{}_{AB}(0)\{1 + [\Delta G_{AB}/4\Delta G^{\ddagger}{}_{AB}(0)]\}^2 \qquad (7)$$

Since eq 4 and 7 behave very similarly in the moderately exoergonic ΔG range,[39] this point is inconsequential to the present discussion. However, we would like to point out that the "evidence for the inverted region" quoted by FH[29] refers to electron transfer between covalently bound reaction partners,[40] while bimolecular reactions in fluid solution usually[41] do not exhibit the inverted region predicted by eq 7.[6,7,9,11,21,42,43]

(b) Instead of calculating k_d from available equations,[19] FH[29] take the average of the values of the rate constants at high exergonicity. We admit that the calculated k_d value may be not very precise. However, the choice made by FH may be more dangerous and, certainly, cannot be generalized because the plateau value for the experimental rate constant may be much lower than the diffusion-controlled value just because of nonadiabaticity reasons.[7,10,11,19,20,24,26] It should also be noted that FH's choice implies the assumption that κ_{AB} is not smaller than 10^{-3}–10^{-4}, while this parameter is then left free to float in their approach (vide infra).

(c) Instead of using eq 6 to try to correlate the electronic transmission coefficients of the cross-reaction and self-exchange reaction, FH[29] use the experimental self-exchange rate constant and leave κ_{AB} and κ_{AA} as unrelated quantities.

Point c is, conceptually, the one that deserves more attention. To further discuss this point, we will try to compare the two approaches with the aid of Scheme I. From the best fit of the log k_{AB} vs. ΔG_{AB} plot of a homogenous series of cross reactions between A and B_1, B_2, B_3, etc. family, one obtains $\Delta G^{\ddagger}{}_{AB}(0)$ and κ_{AB}. From $\Delta G^{\ddagger}{}_{AB}(0)$, using the known $\Delta G^{\ddagger}{}_{BB}$ and eq 5, one can obtain $\Delta G^{\ddagger}{}_{AA}$. From here on, the two approaches differ. We[7,19,25,26,38] (dashed lines, Scheme I) factorize κ_{AB}, making use of the known κ_{BB} and of eq 6 as a working hypothesis, to obtain an "apparent" electronic transmission coefficient, $\kappa_{AA}{}^{app}$. An "apparent" self-exchange rate constant, $k_{AA}{}^{app}$, can then be obtained. FH[29] (dotted line, Scheme I) make use of the experimental self-exchange rate constant to obtain κ_{AA}, which is considered to be completely unrelated to κ_{AB}. Their approach is, of course, quite safe but not very fruitful. We believe that it is much more productive to think about the nonadiabaticity problem of cross-reactions in terms of intrinsic parameters of the reaction partners, even if such an approach is clearly open to criticisms at a quantitative level.[8,10,33,38]

To illustrate this point, we will briefly make reference to the reactions of Co(III) complexes (A) with a series of Ru– and Os–polypyridine complexes (B),[25] whose relevant parameters are given in Table I. A comparison between either $\kappa_{AA}{}^{app}$ and κ_{AA} or $k_{AA}{}^{app}$ and $k_{AA}{}^{exptl}$ (Scheme I) can show whether or not eq 6 is valid. Table I shows that eq 6 is substantially obeyed for $Co(NH_3)_6{}^{3+/2+}$; for $Co(en)_3{}^{3+/2+}$ $k_{AA}{}^{app}$ is definitely higher than $k_{AA}{}^{exptl}$ while the contrary occurs for $Co(bpy)_3{}^{3+/2+}$. The fact that the cross-reaction may exhibit a different degree of nonadiabaticity than that expected on the basis of the correspondent self-exchange reactions has often been remarked on in recent papers.[8,10,38,44-46] Although the reasons why this happens are not yet clear, *any statement of this problem implies, at least at a conceptual level, a relationship among* κ_{AA}, κ_{BB}, *and* κ_{AB}.

In conclusion, the two approaches, rather than "alternate", should be viewed as complementary. Both of them may be useful in different contexts. When the kinetic differences between different A/A$^-$ couples in outer-sphere electron-transfer reactions are sought for, the comparison between parameters derived from their cross-reactions with the same series of homogeneous partners is likely to be more instructive than the comparison between parameters derived from their self-exchange reactions. In fact, when a species behaves nonadiabatically in genuine outer-sphere reactions, its outer-sphere self-exchange may be so slow (because of both nonadiabaticity and activation energy) that alternative pathways[10,11,45,46] (e.g. copenetration of reactants,[47] formation of bridges,[48] etc.) may give the main contribution to the measured self-exchange rate.

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(39) Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140; **1980**, *102*, 3663.
(40) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
(41) "Vestiges" of the inverted region have been found for Ru–polypyridine reactions: Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 241.
(42) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.
(43) Indelli, M. T.; Ballardini, R.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2547.
(44) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
(45) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilasaran, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.
(46) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 3403.
(47) Tembe, B. L.; Fiedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982**, *76*, 1490.
(48) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557.