# Application of the Marcus Cross Relation to Hydrogen Atom Transfer Reactions

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**The transfer of a hydrogen atom—a proton and an electron—is a fundamental process in chemistry and biology. A variety of hydrogen atom transfer reactions, involving iron complexes, phenols, hydroxylamines, ᵗBuOOH, toluene, and related radicals, are shown to follow the Marcus cross relation. Thus, the Marcus theory formalism based on ground-state energetics and self-exchange rates, originally developed for electron transfer processes, is also valuable for hydrogen atom transfer. Compounds that undergo slow proton transfer (C–H bonds) or slow electron transfer (cobalt complexes) also undergo slow hydrogen atom transfer. Limitations of this approach are also discussed.**

Hydrogen atom (H-atom) transfer reactions (Eq. 1) are key steps in a wide range of chemical and biochemical processes.

$$X + H - Y \rightarrow X - H + Y \qquad (1)$$

They are involved in the combustion of hydrocarbons, in large-scale industrial oxidation processes (*1*), in a variety of enzymatic transformations (*2*, *3*), and in biochemical protections against reactive oxygen species (ROS) (*4*). Because a hydrogen atom is a proton and an electron, these are one class of proton-coupled electron transfer reactions, which are increasingly implicated in biological systems, from enzymatic oxygen production to charge transport in DNA (*3*, *5–7*). H-atom transfer reactions of organic radicals have been intensively studied, and thousands of rate constants have been determined (*8*). The rate constants correlate linearly with reaction enthalpies, but only within classes of "similar" radicals [the Polanyi relation (*9*)]. Marked variations in rates are observed between different classes of radicals; for instance, $H^\bullet$-abstraction reactions involving O–H bonds are orders of magnitude faster than those involving C–H bonds at similar driving forces. This is one reason why natural antioxidants use reactive O–H bonds (as in vitamin C and vitamin E) rather than C–H bonds.

We report here that rate constants for a range of H-atom transfer reactions follow the Marcus cross relation (*10*, *11*):

$$k_{XY} = \sqrt{k_{XX}k_{YY}K_{XY}f_{XY}} \qquad (2)$$

Marcus theory has been previously applied to proton transfer (*12*, *13*), hydride transfer (*14*), and methyl transfer ($S_N2$) reactions (*12*, *15*), but it was derived for electron transfer between weakly coupled reagents and its applicability is not widely established for reactions that involve bond making and breaking. This is the first test for solution-phase hydrogen atom transfer reactions (*16*, *17*), and its success provides new insights. In this formalism, reaction rates are a function of thermodynamic driving force (the equilibrium constant $K_{XY}$) and intrinsic barriers [the frequency factor, $f_{XY}$, is typically close to 1 (*10*)]. The intrinsic barrier reflects the propensity for reaction in the absence of driving force, appearing in Eq. 2 via the self-exchange rates $k_{XX}$ and $k_{YY}$. Equation 2 is derived from the classical Marcus equation and relies on the assumption—the additivity postulate—that the intrinsic barrier to a nondegenerate reaction is the mean of the barriers for the constituent self-exchange reactions. Although the cross relation is now viewed as an overly simplistic treatment for electron transfer (*18*), it was instrumental in the development of the field.

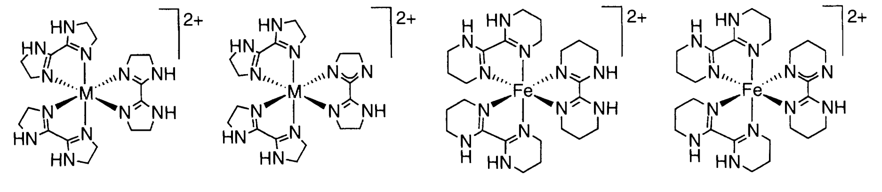
Three related sets of tris(α-diimine) metal complexes were used in this study: iron complexes of 2,2′-biimidazoline ($H_2$bim) and 2,2′-bi(tetrahydro)pyrimidine ($H_2$bip) and cobalt complexes of $H_2$bim (Scheme 1). The divalent metal species, $[M(H_2L)_3](ClO_4)_2$, can be oxidized and deprotonated to give trivalent $[M(HL)(H_2L)_2](ClO_4)_2$ (*19–21*). These compounds, abbreviated $M^{II}(H_2L)$ and $M^{III}(HL)$, differ by a single H-atom. The N–H bond dissociation energies (BDEs)—the enthalpy of removal of $H^\bullet$ from $M^{II}(H_2L)$ to give $M^{III}(HL)$—were determined from the acidities ($pK_a$) and redox potentials ($E°′$) (*22*) with a thermochemical cycle as previously described for $Fe^{II}(H_2bim)$ (Table 1) (*23*). The rate of H-atom self-exchange between $Fe^{II}(H_2bip)$ and $Fe^{III}(Hbip)$ was measured by nuclear magnetic resonance (NMR), following the procedure used for $Fe^{II}(H_2bim)$ + $Fe^{III}(Hbim)$ (*19*). Broadening of the $^1H$ NMR signals of $Fe^{II}(H_2bip)$ on addition of $Fe^{III}$ (Hbip) gives a rate constant of $(1.3 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$, slightly faster than that found for $Fe^{II}(H_2bim)$, $(5.8 \pm 0.6) \times 10^3\ M^{-1}\ s^{-1}$.

$Fe^{III}(Hbim)$ abstracts H-atoms from hydroxylamines that have weak O–H bonds, analogous to previously reported oxidations of hydrocarbons (*23*). Reaction with *N*-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPO-H) gives the 2,2,6,6-tetramethyl-piperidinoxyl radical ($TEMPO^\bullet$; Scheme 2). This reaction is enthalpically downhill by 6 ± 2 kcal/mol, based on the BDEs (Table 1). $Et_2NOH$ is similarly oxidized by $Fe^{III}(Hbim)$, yielding $CH_3CH{=}N(Et)O$ by stepwise removal of two H-atoms. In the reverse direction, 2,4,6-tri-*t*-butylphenoxyl radical ($^tBu_3C_6H_2O^\bullet$) (Scheme 2) and benzyl radical (*24*) oxidize $Fe^{II}(H_2bim)$ to $Fe^{III}(Hbim)$, consistent with the stronger X–H bonds in these species (Table 1). Metal-mediated oxidations of O–H bonds are well known (*25*); the reverse process, oxidation of a metal center by an organic radical, is rare but has been invoked in enzymatic mechanisms (*2*).

The iron-$H_2$bip and cobalt-$H_2$bim systems also react with hydroxylamines, phenols, and isolable oxyl radicals. The N–H bond strengths of the reduced metal complexes are comparable to that of TEMPO–H, so an equilibrium is established:

$$[M^{II}(H_2L)_3]^{2+} + TEMPO^\bullet \overset{K_{eq}}{\rightleftarrows} [M^{II}(HL)(H_2L)_2]^{2+} + TEMPO\text{-}H \qquad (3)$$

The entropy change ($\Delta S$) for Scheme 2 and Eq. 3 and related reactions should be quite small, so the free energy change ($\Delta G°$) is taken to be equal to the enthalpy change $\Delta H°$ (and equal to $-RT\ln K_{eq}$, where $K_{eq}$ is the equilibrium constant). $\Delta H°$ is the difference between the strengths of the bonds



$M^{II}(H_2bim)$ $M^{III}(Hbim)$ $Fe^{II}(H_2bip)$ $Fe^{III}(Hbip)$

M = Fe, Co

**Scheme 1.**

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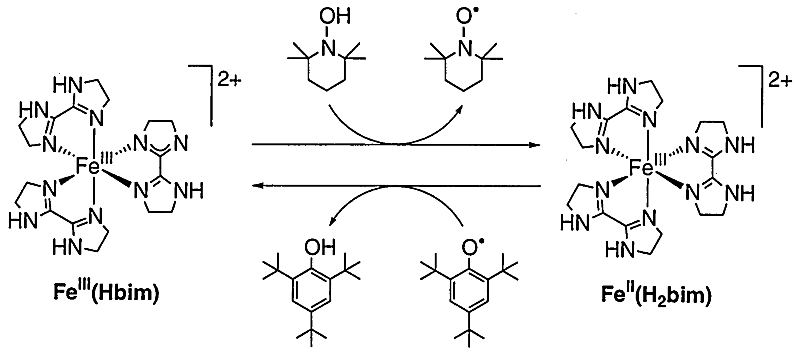
being made and broken. The equilibrium constants for Co($H_2$bim) (0.01 by optical spectroscopy) and Fe($H_2$bip) (0.3 from forward and reverse reaction rate constants) therefore provide independent confirmation of the electrochemically determined BDEs.

Rate constants were determined for 12 different combinations of a metal complex and a hydroxyl compound or an organic radical (Table 2). The reactions were carried out in air-free acetonitrile solutions, $\sim 10^{-4}$ M in metal complex and under pseudo–first-order or mixed second-order conditions, with an Olis stopped flow apparatus equipped with a rapid scanning optical spectrophotometer. For all reactions, initial and final concentrations of inorganic species were determined from the appropriate molar extinction coefficients. In most cases, $^1$H NMR analysis allowed the expected products to be confirmed and quantified. All of the reactions in Table 2 likely occur by one-step H-atom transfer, alternatively described as proton-coupled electron transfer. Other pathways involving stepwise transfer—proton then electron or vice versa—are less likely on the basis of the relevant p$K_a$ (where $K_a$ is the acid constant) and redox potentials and estimates of electron transfer rates from Marcus theory (*20*, *26*).

The data are available (Table 1) to test the Marcus cross relation (Eq. 2) for nine H-atom transfer reactions involving the iron complexes. Observed and calculated rate constants are compared in Table 2 and in Fig. 1, in which the line with unit slope and zero intercept represents the ideal fit. Also included in Table 2 and Fig. 1 are three organic H-atom transfer reactions for which self-exchange rate constants are known: $^t$BuO$^•$ + $PhCH_3$, $^t$BuOO$^•$ + $PhCH_3$, and $^t$Bu$_3$C$_6$H$_2$O$^•$ + $^t$BuOOH (the ▲ symbols in Fig. 1). The uncertainties in the computed cross reaction rate constants are estimated to be plus or minus an order of magnitude, primarily on the basis of uncertainties in the bond strengths. The agreement between experimental and calculated rate constants is quite good for observed rate constants that span nine orders of magnitude.

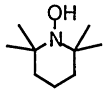
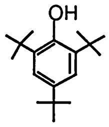
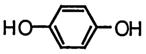
A key feature of this study is that it spans a wide range of driving force and intrinsic barriers, with equilibrium constants varying over $10^{18}$ and self-exchange rate constants over a range of $10^9$. For instance, the two reactions Fe$^{III}$(Hbim) + TEMPO-H and Fe$^{II}$($H_2$bim) + $PhCH_2^•$ occur with the same rate constant because the $\sim 10^6$ smaller $K_{eq}$ for the former is balanced by the $\sim 10^6$ smaller $k_{XX}$ for $PhCH_2^•$/$PhCH_3$ versus TEMPO/TEMPO-H. The self-exchange reactions are quite different in appearance from the cross reactions. In many of the previous studies of atom and group transfer reactions, the self-exchange reactions have resembled the cross reactions, and it has been suggested that such similarities are required for successful application of the cross relation (*14*). The cross reactions examined here encompass both metal-containing and all-organic reactions and involve N–H, O–H, and/or C–H bonds.

Cross reactions involving Co-biimidazoline complexes are orders of magnitude slower than those of the two Fe systems, even though the N–H bond strength is intermediate. For example, Fe$^{II}$($H_2$bim) and Fe$^{II}$($H_2$bip) are oxidized by $^t$Bu$_3$C$_6$H$_2$O$^•$ with second-order rate constants of $6.8 \times 10^5$ and $>10^7$ $M^{-1}$ $s^{-1}$, whereas the analogous reaction of Co$^{II}$($H_2$bim) occurs at 38 $M^{-1}$ $s^{-1}$. The slow reactions of the Co complexes result from the high intrinsic barrier to self-exchange; a rate constant of about $10^{-6}$ $M^{-1}$ $s^{-1}$ can be estimated with the Marcus cross relation. Unfortunately, direct determination of this rate constant is not possible because H-atom exchange between Co$^{II}$($H_2$bim) and Co$^{III}$ (Hbim) occurs by a different mechanism. An inner-sphere path-



**Scheme 2.**

**Table 1.** Properties of reagents HX/X$^•$.

| HX | BDE (X–H) (kcal mol$^{-1}$) | Reference | $k_{SE}$ ($M^{-1}$ $s^{-1}$) (298 ± 2 K) | Reference |
|---|---|---|---|---|
| Fe$^{II}$($H_2$bim) | 76 ± 2 | (*23*) | $(5.8 \pm 0.6) \times 10^3$* | (*19*) |
| Fe$^{II}$($H_2$bip) | 71 ± 1 | This work | $(1.3 \pm 0.2) \times 10^4$* | This work |
| Co$^{II}$($H_2$bim) | 72 ± 3 | This work | Not determined | |
| $^t$Bu$_2$NOH | 68.2 ± 1 | (*36*) | $1.2 \times 10^2$† | (*37*) |
| Et$_2$NOH | 75.9 ± 1 | (*36*) | $1.2 \times 10^2$‡ | |
|  | 69.7 ± 1 | (*36*) | $(7 \pm 1) \times 10^1$ | (*20*) |
|  | 81.2 ± 1 | (*19*) | $2.2 \times 10^2$§ | (*19*) |
|  | 81.5 ± 1 | (*26*) | $3 \times 10^4$‖ | (*38*) |
| $^t$BuOH | 105 ± 1 | (*19*) | $\sim 3 \times 10^4$¶ | (*19*) |
| $^t$BuOOH | 89 ± 1 | (*19*) | $5 \times 10^2$# | (*19*) |
| $PhCH_2$–H | 90 ± 1 | (*19*) | $\sim 4 \times 10^{-5}$** | (*19*) |

*MeCN solvent. †$C_6H_5Cl$ solvent. ‡$k_{SE}$ ($^t$Bu$_2$NOH/$^t$Bu$_2$NO$^•$). §$CCl_4$ solvent. ‖$k_{SE}$(3,6-$^t$Bu$_2$catechol/3,6-$^t$Bu$_2$orthosemiquinone radical) in $CCl_4$ solvent. ¶$^t$BuO$^•$ + $^t$Bu$_3$COH in $^t$BuOO$^t$Bu solvent. #$k$($^t$BuOO$^•$ + $^s$BuOOH) in $^i$C$_5$H$_{12}$. **$C_6H_5CH_3$ solvent.

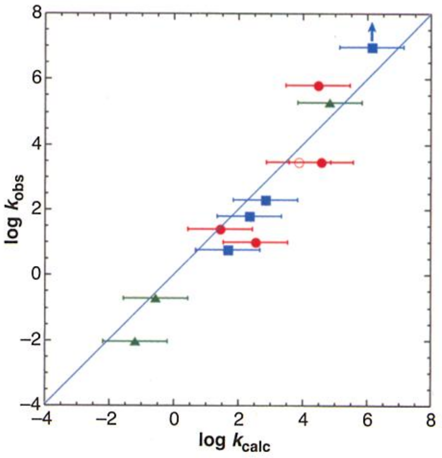


**Fig. 1.** Comparison between experimentally determined and predicted H$^•$-abstraction rate constants. A line of unit slope is drawn that represents perfect agreement between experiment and theory. Data from Table 2 for reactions of Fe$^{II}$($H_2$bim) or Fe$^{III}$(Hbim) (●), Fe$^{II}$($H_2$bim) + $PhCH_2^•$ (○), Fe$^{II}$($H_2$bip) or Fe$^{III}$(Hbip) (■), and the all-organic reactions (▲); the $k_{obs}$ of $10^7$ for the upper right point is a minimum value.

**Table 2.** Observed and calculated rate constants for hydrogen atom transfer reactions.

| Reactants | $K_{12}$ | $k_{12}$(obs) per $H^{\bullet}$* | $k_{12}$(calc)† |
|---|---|---|---|
| $Fe^{III}(Hbim) + HOC_6H_4OH$ | $9 \times 10^{-5}$ | $28 \pm 6$ | 30 |
| $Fe^{III}(Hbim) + Et_2NOH$ | 1 | $11 \pm 2$ | $3 \times 10^{2}$ |
| $Fe^{III}(Hbim)$ + TEMPO-H | $4 \times 10^{4}$ | $(3.1 \pm 0.1) \times 10^{3}$ | $4 \times 10^{4}$ |
| $Fe^{II}(H_2bim) + {}^{t}Bu_3C_6H_2O^{\bullet}$ | $6.5 \times 10^{3}$ | $(6.8 \pm 0.2) \times 10^{5}$ | $3 \times 10^{4}$ |
| $Fe^{II}(H_2bim) + PhCH_2^{\bullet}$‡ | $2 \times 10^{10}$ | $\sim 3 \times 10^{3}$‡ | $8 \times 10^{3}$ |
| $Fe^{III}(Hbip)$ + TEMPO-H | 3§ | $(2.2 \pm 0.2) \times 10^{2}$ | $7 \times 10^{2}$ |
| $Fe^{II}(H_2bip) + TEMPO^{\bullet}$ | $3 \times 10^{-1}$§ | $70 \pm 2$ | $2 \times 10^{2}$ |
| $Fe^{II}(H_2bip) + {}^{t}Bu_2NO^{\bullet}$ | $9 \times 10^{-3}$ | $6.3 \pm 0.2$ | 50 |
| $Fe^{II}(H_2bip) + {}^{t}Bu_3C_6H_2O^{\bullet}$ | $3 \times 10^{7}$ | $>10^{7}$ | $1 \times 10^{6}$ |
| $Co^{II}(H_2bim) + TEMPO^{\bullet}$ | $1 \times 10^{-2}$§ | $(2.8 \pm 0.6) \times 10^{-5}$ | NA |
| $Co^{III}(Hbim) + HOC_6H_4OH$ | $1 \times 10^{-7}$ | $(1.5 \pm 0.5) \times 10^{-3}$ | NA |
| $Co^{II}(H_2bim) + ArO^{\bullet}$ | $6 \times 10^{6}$ | $38 \pm 5$ | NA |
| ${}^{t}BuO^{\bullet} + PhCH_3$ | $1 \times 10^{11}$ | $2 \times 10^{5}\|$¶ | $7 \times 10^{4}$ |
| ${}^{t}BuOO^{\bullet} + PhCH_3$ | 0.2 | $1 \times 10^{-2}\|$# | $6 \times 10^{-2}$ |
| $ArO^{\bullet} + {}^{t}BuOOH$ | $2 \times 10^{-6}$ | $2 \times 10^{-1}\|$** | $3 \times 10^{-1}$ |

*$M^{-1}\,s^{-1}$, 298 K, $CH_3CN$ solvent; statistical corrections applied where necessary. †From Eq. 2, data from Table 1; NA, not available. ‡From (*24*). § Calculated from forward and reverse rate constants (Fe) or from equilibrium concentrations (Co) rather than from $K_{12} \cong e^{-\Delta BDE/RT}$. ‖From (*8*). ¶$C_6H_6/{}^{t}BuOOBu^{t}$solvent. #$C_6H_5CH_3$ solvent. **$C_6H_6$ solvent.

way involving ligand exchange was confirmed by mass spectrometry of a solution of $Co^{III}(Hbim)$ and $Co^{II}(H_2bim)$-$d_{24}$ (deuterated at the aliphatic ligand positions). A high barrier for $Co^{II}(H_2bim)/Co^{III}(Hbim)$ interchange is expected on the basis of the large intrinsic barriers traditionally observed for electron transfer between high-spin Co(II) and low-spin Co(III) (*10*, *27*). Indeed, the electron transfer self-exchange rate between $Co^{II}(H_2bim)$ and $Co^{III}(H_2bim)$ was determined to be about $10^{-6}$ $M^{-1}$ $s^{-1}$ by reaction of $Co^{II}(H_2bim)$ with $Fe^{III}(H_2bim)$ and application of the Marcus cross relation for electron transfer. With a large intrinsic barrier to electron transfer, it is reasonable that the Co system will have a large barrier to H-atom transfer (proton-coupled electron transfer).

The application of the cross relation to H-atom transfer reactions described here, although successful, overlooks a number of complications. It ignores the energetics of assembly of the precursor complex, which for electron transfer is typically limited to electrostatic effects (*28*) but for H-atom transfer reactions will include orientation requirements and steric interactions (*29*). In addition, hydrogen bonds may be formed or broken in making the precursor complex, which could have a substantial influence (*30*). However, the benzyl radical and toluene reactions, where hydrogen bonding is minimal, follow the cross relation as closely as the reactions that likely involve hydrogen bonds. The Marcus approach also assumes that the reactive nuclear configurations are similar in the self-exchange and cross reactions, which may not be the case (*31*). Polar effects, a common feature of organic H-atom transfer reactions due to charge variations in transition states (*9*), are not easily accounted for in this treatment. Finally, the treatment used here ignores the possibility of nonadiabatic transfer of either the electron or the proton or both, which are key features of current theoretical treatments (*5*, *6*, *32*, *33*). The rough agreement suggests that these effects are either not very large or that they are moderated by the averaging implicit in the cross relation (*10*, *11*). For instance, Eq. 2 will hold even if the reactions have nonadiabatic character when the electronic coupling energy $(H_{AB})_{12} = [(H_{AB})_{11}(H_{AB})_{22}]^{1/2}$ (*11*).

The success of the Marcus cross relation for a variety of H-atom transfer reactions, predicting rate constants within one to two orders of magnitude, signals a new approach to understanding these important chemical processes. The much faster reactions of O–H versus C–H bonds reflect the roughly $10^8$ difference in self-exchange rate constants. The Polanyi relation is seen as a corollary of the Marcus relation and therefore Marcus theory, holding when self-exchange rates are similar (*34*). Our previous findings that H-atom abstractions by transition metal compounds follow the Polanyi relation in the same class as oxygen radicals (*35*) are explained by the similarity in the self-exchange rates. The unusually slow reactions of the cobalt complexes reported above suggest that systems with high inner-sphere barriers to electron transfer will also have high barriers to hydrogen atom transfer (proton-coupled electron transfer).

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21. Caution: These perchlorate salts are explosive and should be handled with caution and in small quantities.
22. All measurements were carried out in $CH_3CN$ (V versus $Cp_2Fe$). $Fe^{II}(H_2bim)$: $pK_a = 17.5 \pm 0.5$; $E°' = -0.31 \pm 0.05$ V. $Fe^{II}(H_2bip)$: $pK_a = 17.5 \pm 0.2$; $E°' = -0.55 \pm 0.05$ V. $Co^{II}(H_2bim)$: $pK_a = 18.8 \pm 0.3$; $E°' = -0.6 \pm 0.1$ V. BDE $= 2.3RT(pK_a) + FE°' + 59.5$ kcal $mol^{-1}$.
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26. E.g., for $Fe^{II}(H_2bim) + {}^{t}Bu_3C_6H_2O^{\bullet}$ (Scheme 2), neither initial proton transfer ($\Delta G° \cong 45$ kcal $mol^{-1}$) nor initial electron transfer ($\Delta G^{\ddagger}_{e} \cong 13$ kcal $mol^{-1}$ from Marcus theory) is consistent with the experimental barrier $\Delta G^{\ddagger} = 8.4$ kcal $mol^{-1}$.
27. The average Co–N bond distances (derived from x-ray crystal structures) lengthen ~0.2 Å upon oxidation of $Co^{II}(H_2bim)$ to $Co^{III}(H_2bim)$ compared with 0.1 Å for the Fe-$H_2$bim system (*20*).
28. Electrostatic work is required to bring the cationic reagents together in the $Fe(H_2L)/Fe(HL)$ self-exchange reactions [~1.3 kcal $mol^{-1}$ (*10*, *11*, *19*)], but there is no such work in the cross reactions. Correcting the self-exchange rates for this work would lower the $k_{calc}$ values by a factor of 3 (0.5 log unit in Fig. 1).
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