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# Slow Electron Transfer Reactions Involving Tetraisopropylhydrazine

Stephen F. Nelsen,*,† Rustem F. Ismagilov,† Ling-Jen Chen,†
Jennifer L. Brandt,‡ Xi Chen,‡ and Jack R. Pladziewicz*,‡

*S. M. McElvain Laboratories of Organic Chemistry*
*Department of Chemistry, University of Wisconsin*
*Madison, Wisconsin 53706-1396*
*Department of Chemistry, University of Wisconsin*
*Eau Claire, Wisconsin 54702*

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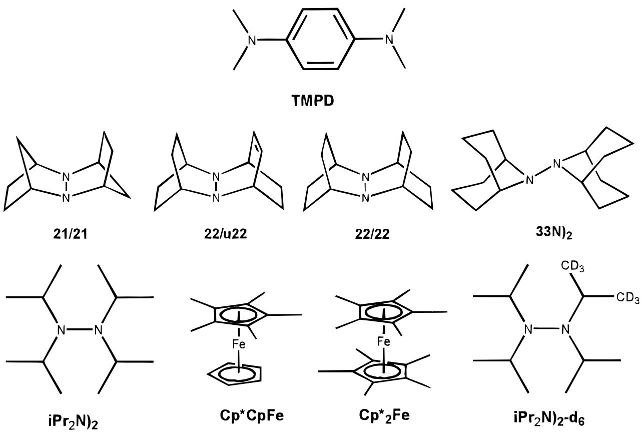
**Chart 1**



Marcus pointed out in 1956 that the fundamental parameter to know for predicting outer-sphere electron transfer (ET) activation free energies is $\lambda$, the vertical free energy gap between a non-interacting pair consisting of a neutral species $\mathbf{M}^0$ and its own radical ion ($\mathbf{M}^+$ or $\mathbf{M}^-$) in solution, and the same pair in which an electron has been transferred between the two components without allowing any relaxation.[1] If the relaxed, solvated neutral and radical cation are designated by **n** and **c**, and the charge present is shown as a superscript, this energy gap for vertical "self-ET" between $\mathbf{n}^0$ and $\mathbf{c}^+$ may be written as the sum of the relaxation energies for cationic and neutral species (eq 1).[2] $\lambda$ corresponds to 4 times the thermal barrier for ET,

$$\lambda = \Delta G_{\mathrm{rel}}(\mathrm{cat}) + \Delta G_{\mathrm{rel}}(\mathrm{neu}) = [\Delta G_{\mathrm{f}}(\mathbf{n}^+) - \Delta G_{\mathrm{f}}(\mathbf{c}^+)] + [\Delta G_{\mathrm{f}}(\mathbf{c}^0) - \Delta G_{\mathrm{f}}(\mathbf{n}^0)] \quad (1)$$

assuming that ET is adiabatic. This concept has remained essentially unchanged for 40 years, although more modern ET theory has introduced other parameters which are also important in determining the ET rate constant.[1] $\lambda$ is assumed to be the sum of a solvation term, $\lambda_{\mathrm{out}}$, which is determined by molecular size and the solvent employed, and a solvent-independent structural reorganization term, $\lambda_{\mathrm{in}}$. $\lambda_{\mathrm{in}}$ is rather small compared to $\lambda_{\mathrm{out}}$ for many aromatic organic molecules, which results in self-ET rate constants $k_{11}$ (rate constants reported here are at 25 °C in $CH_3CN$ containing 0.10 M tetrabutylammonium perchlorate) above $10^8$ $M^{-1}$ $s^{-1}$ for many aromatic compounds.[3] For the particularly well studied tetramethyl-*p*-phenylenediamine, TMPD, $k_{11}$ is $1.5 \times 10^9$ $M^{-1}$ $s^{-1}$.[4] $\lambda_{\mathrm{in}}$ increases as the structural change between $\mathbf{n}^0$ and $\mathbf{c}^+$ increases, and tetraalkylhydrazines undergo especially large structural changes upon electron loss, resulting in far higher $\lambda_{\mathrm{in}}$ values and much smaller $k_{11}$ values.[5] It is necessary to have mutual stability of both oxidation states for direct measurement of $k_{11}$, which requires special alkyl groups for tetraalkylhydrazines. Several bis(bicycloalkyl) hydrazines which give isolable radical cations because of Bredt's rule protection from $C_\alpha$−H cleavage[6] have been made, the size of their structural changes upon electron removal has been documented,[5] and $k_{11}$ values have been measured by slow exchange region NMR line broadening.[7] The nitrogen lone pair, lone pair dihedral angle, $\theta$, is near 0° for **21/21** and **22/u22**, which have the highest $k_{11}$ values reported, $1.85 \times 10^4$ and $1.21 \times 10^4$ $M^{-1}$ $s^{-1}$, respectively.[7c] **21/21** has $k_{11}$ 26 times that for the slightly twisted **22/22**[7] and 8.4 times that estimated for the $\theta = 180°$ hydrazine **33N)₂** from NMR line broadening studies in $CD_2Cl_2$.[8] $\lambda_{\mathrm{in}}$ should increase significantly when $\theta$ changes greatly between $\mathbf{n}^0$ and $\mathbf{c}^+$, as shown by measurements of the enthalpy portion of $\Delta G_{\mathrm{rel}}(\mathrm{cat})$ using photoelectron spectroscopy and high-pressure mass spectrometry,[9] but how large the effect might be remained unmeasured until this work. By these criteria, the $\theta \approx 90°$ tetraisopropylhydrazine, **iPr₂N)₂**, should have a larger $\lambda$ and lower $k_{11}$. We recently showed by isolating **iPr₂N)₂**$^+$ that it is not necessary to have Bredt's rule protection to produce isolable hydrazine radical cations; four α-branched substituents provide sufficient kinetic protection from $C_\alpha$−H bond cleavage reactions.[10] The formal reduction potential for **iPr₂N)₂**$^+$ of +0.26 V (vs a saturated calomel electrode in acetonitrile containing 0.1 M tetraethylammonium perchlorate, abbreviated $E°'$ below) is high enough for its radical cation to be a convenient oxidant for other compounds, allowing the cross-ET rate constant $k_{12}$ to be measured by stopped-flow techniques, as we have previously reported for other ET reactions involving hydrazines.[8,11] Marcus showed that if ET is assumed to be adiabatic and $\lambda_{12}$ for a cross-ET is assumed to be the average of $\lambda_{11}$ and $\lambda_{22}$ for the two components, $k_{12}$ is given by eqs 2 and 3, where $Z_{12}$ is the preexponential factor for the mixed ET.[12] Using eqs

$$k_{12}(\mathrm{calc}) = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (2)$$

$$\ln f_{12} = (\ln K_{12})^2/[4 \ln(k_{11}k_{22}/Z_{12}{}^2)] \quad (3)$$

2 and 3 with $Z_{12} = 10^{11}$ $M^{-1}$ $s^{-1}$ works rather well for ET reactions between a wide variety of transition metal coordination complexes for which the $k_{ii}$ values were independently determined.[1] Equation 2 is quite insensitive to the $Z_{12}$ employed unless $K_{12}$ is very different from 1.[8] Nevertheless, one might expect deviations when the ET partners differ greatly electroni-

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[†] UW−Madison.

[‡] UW−Eau Claire.

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(8) (a) Nelsen, S. F.; Chen, L.-J.; Ramm, M. T.; Voy, G. T.; Powell, D. R.; Accola, M. A.; Seehafer, T. R.; Sabelko, J. J.; Pladziewicz, J. R. *J. Org. Chem.*, in press. (b) The effect is largest for the smaller $f_{12}$. Using **22/u22** as reductant, use of $Z_{12} = 10^9$ $M^{-1}$ $s^{-1}$ increases $k_{11}$(calc) by 59%, and use of $10^{13}$ decreases it by 36%. The corresponding changes are ≤+12% and −9% for the reductants with smaller ΔΔ*G*°.

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**Table 1.** Comparison of Stopped-Flow Cross Rate Studies using **iPr$_2$N)$_2$**$^+$ as Oxidant with the Directly Measured Value for **iPr$_2$N)$_2$**$^{0/+}$

| reductant | $\Delta G^0$, kcal/mol | $k_{22}$(obs), M$^{-1}$ s$^{-1}$ | $k_{12}$(obs), M$^{-1}$ s$^{-1}$ | $f_{12}$(calc) | $k_{11}$(calc), M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| TMPD | −3.2 | $1.5 \times 10^9$ [a] | $(1.6 \pm 0.1) \times 10^3$ | 0.82 | $5.1 \times 10^{-4}$ |
| Cp*CpFe | −3.1 | $8.5 \times 10^6$ [b] | $(1.2 \pm 0.1) \times 10^4$ | 0.84 | $18 \times 10^{-4}$ |
| Cp*$_2$Fe | −8.5 | $2.9 \times 10^7$ [c] | $(4.9 \pm 0.6) \times 10^4$ | 0.29 | $4.0 \times 10^{-4}$ |
| **21/21** | −5.8 | $1.9 \times 10^4$ [b] | $(2.6 \pm 0.02) \times 10^2$ | 0.35 | $3.5 \times 10^{-4}$ |
| **33N)$_2$** | −6.2 | $2.2 \times 10^3$ [b] | $(1.1 \pm 0.2) \times 10^2$ | 0.26 | $2.6 \times 10^{-4}$ |
| **22/u22** | −11.6 | $1.2 \times 10^4$ [c] | $(1.1 \pm 0.1) \times 10^4$ | 0.15 | $2.3 \times 10^{-4}$ |
| **22/22** | −18.2 | $7.0 \times 10^2$ [d] | $(3.2 \pm 0.2) \times 10^5$ | 0.01 | $6.4 \times 10^{-4}$ |
| | | | | | $6.0 \times 10^{-4}$ (av) |
| **iPr$_2$N)$_2$-$d_6$** | 0 | $3.0 \times 10^{-3}$ | | | $30 \times 10^{-4}$ (obs) |

[a] From ref 4b. [b] From ref 8a. [c] From ref 11. [d] From refs 7.

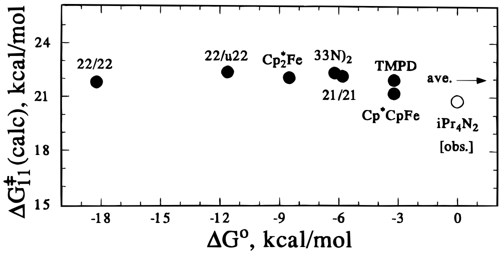

**Figure 1.** Plot of $\Delta G^{\ddagger}_{11}$(calc) versus $\Delta G°$ for the reduction of **iPr$_2$N)$_2$**$^+$ by the seven reductants of Table 1, along with the observed value.

cally, because the parameters $V$ and $h\nu_{in}$ used in more modern, diabatic ("nonadiabatic") ET theory[1] ought to vary, causing the preexponential factors for $k_{11}$ and $k_{22}$ to differ. It is not at all clear how $Z_{12}$ ought to be predicted in such a case. Hydrazines, ferrocenes, and TMPD have all been argued to have significantly diabatic ET,[7c] but eqs 2 and 3 with $Z_{12} = 10^{11}$ M$^{-1}$ s$^{-1}$ have been shown to work as well for tetraalkylhydrazine−methylated ferrocene cross-ET reactions[8,11] as they do for reactions between transition metal coordination complexes. The most stringent tests of the $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$ assumption occur when the components differ greatly in $\lambda_{in}$, so that $k_{22}$ is very different from $k_{11}$. This effect has been examined in this work, where TMPD, methylated ferrocenes Cp*CpFe and Cp*$_2$Fe, and the four hydrazines shown above have been used as reductants of **iPr$_2$N)$_2$**$^+$. The cross ET rate constants, $k_{12}$(obs), for these reactions are summarized in Table 1, and a plot of the self-ET activation free energy, $\Delta G^{\ddagger}_{11}$(calc), versus cross-reaction free energy, $\Delta G°$, is shown in Figure 1. In spite of great differences in the intrinsic reducing agent reactivity (the range of reducing agent $k_{22}$ values is a factor of $2.1 \times 10^6$), the $k_{11}$(calc) values derived for **iPr$_2$N)$_2$** from $k_{12}$(obs) are very similar, agreeing within a factor of 8. Moreover, $k_{11}$(calc) is quite insensitive to the substantial differences in electronic and molecular structure of the reductants, and there is no significant trend with reaction $\Delta G°$ for the $k_{11}$(calc) values obtained. As observed previously,[8] cross-reactions employing Cp*$_2$Fe produce slightly lower $k_{11}$(calc) values than do reactions using Cp*CpFe.

The self-exchange ET for **iPr$_2$N)$_2$**$^{0/+}$ is so slow that direct measurement of $k_{11}$ was possible. Acetone-$d_6$ was employed to introduce one CH(CD$_3$)$_2$ group, producing **iPr$_2$N)$_2$-$d_6$**, and the concentration of labeled neutral material was monitored as a function of time by both $^2$H- and $^1$H-NMR upon addition of unlabeled radical cation. $k_{11}$(obs) values for **iPr$_2$N)$_2$**$^{0/+}$ were determined from four kinetic runs to be $(3.0 \pm 0.3) \times 10^{-3}$ M$^{-1}$ s$^{-1}$, 5.0 times the average $k_{11}$(calc) value.

This work extends the total $k_{11}$ range measured for tetra-α-branched tetraalkylhydrazines to a factor of $5.6 \times 10^6$, a $\Delta G^{\ddagger}$ difference of 9.2 kcal/mol, between the $\theta \approx 0°$ compound **21/21** and the $\theta \approx 90°$ **iPr$_2$N)$_2$**. This would correspond to a $\lambda_{in}$ difference of 36.8 kcal/mol if the preexponential factor and $\lambda_{out}$ were the same for both hydrazines (which might not be the case). The effect of $\theta$ on $k_{11}$, and thus presumably on $\lambda_{in}$, for hydrazines is clearly much larger than that calculated by the AM1 method.[2b] Our work demonstrates that the use of Marcus cross rate theory produces $k_{11}$(calc) values for **iPr$_2$N)$_2$**$^{0/+}$ within a factor of 13 of the correct value for compounds which differ tremendously in $k_{22}$, range electronically from being diaminobenzenes to two-atom $\pi$-centered to iron-centered radical cations, and range sterically from having an unsubstituted cyclopentadienyl $\pi$-system to having a dinitrogen $\pi$-system which is blocked by the presence of four α-branched alkyl substituents. Electronic factors appear to be surprisingly unimportant in determining $k_{12}$(obs), and the reaction with the aromatic amine TMPD, which has $k_{22}$(obs) $5 \times 10^{11}$ times faster than **iPr$_2$N)$_2$**, gives a $k_{11}$(calc) value which is closer to the experimental value than do reactions with three of the four hydrazines studied, which are far closer in structure to **iPr$_2$N)$_2$**. Higher $k_{11}$(obs) values than $k_{11}$(calc) from cross rate studies have resulted for all hydrazines studied.[8,11] The smallest ratios of $k_{11}$(obs) to $k_{11}$(calc) have been found for reactions involving Cp*CpFe: the ratios are 2.2 for **33N)$_2$**, 2.0 for **22/u22**, and from this work, 1.7 for **iPr$_2$N)$_2$**. We lack an internally self-consistent explanation[13] for why $k_{11}$(calc) values are smaller than those obtained by direct measurement.

Recent work concludes[14] that several classes of organic electron transfer reactions occur by inner-sphere mechanisms, including self-exchange reactions of alkyl halides,[15] aromatic radical anion/neutral exchange,[15] and aromatic nitration.[16] This work compels us to consider the possibility that the reactions considered here are influenced by partial bond formation in the transition state sufficient for their classification as inner-sphere. Several characteristics of the **iPr$_2$N)$_2$** reactions make this unlikely. In addition to there being no direct evidence for bonded intermediates, the nitrogen atoms of **iPr$_2$N)$_2$** are sterically hindered by the isopropyl groups in a manner that greatly restricts close approach of the reactants used in this study. Moreover, the agreement of the directly measured $k_{11}$ for **iPr$_2$N$_2$** with those derived from the varied cross-reactions would require that all of the cross-reactions have approximately the same degree of bond formation in the transition state and be slightly less bonded than the **iPr$_2$N)$_2$** self-exchange. This would be a remarkable coincidence and seems unlikely. However, given the importance of this mechanistic question, even more stringent tests of the assumptions implicit in our treatment of the **iPr$_2$N)$_2$** reactions are being sought and will be discussed in the future.

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(13) Lowering $Z_{12}$ slightly raises $k_{11}$(calc), but the effect is small: the average $k_{11}$(calc) for the data of Table 1 is $6.9 \times 10^{-4}$ using $Z_{12}$ of $10^{10}$, and $8.7 \times 10^{-4}$ using $10^9$. Differing precursor complex equilibrium constants would also affect the rate, but they would have to be rather constant between $\Delta G°$ of −3 and −18 kcal/mol, yet all differ significantly from the value at $\Delta G° = 0$, which appears unlikely. Supporting electrolyte was not used in the NMR measurement.

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