Intrinsic Electron Transfer Reactivities

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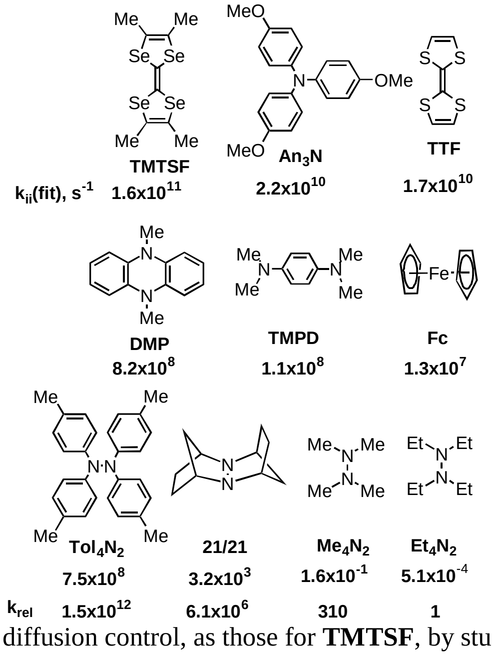
Marcus introduced the idea of intrinsic rate constants for electron transfer in the middle 1950s. If k_{ii} is the intrinsic rate constant for self-exchange of neutral compound $\boldsymbol{I^0}$ with its radical cation $\boldsymbol{I^+}$, as shown below,

$$\boldsymbol{I^0} + \boldsymbol{I^+} \overset{k_{ii}}{\rightleftharpoons} \boldsymbol{I^+} + \boldsymbol{I^0}$$

the rate constant for electron transfer between $\boldsymbol{I^+}$ and a different neutral compound $\boldsymbol{J^0}$ (described as a cross electron transfer) is surprisingly simple. When one component is neutral so no work terms are present, and if it is assumed that the reaction is adiabatic and the barrier is the crossover point of parabolas representing starting materials and product that are displaced by the driving force of the reaction, the cross rate constant k_{12} is shown:

$$k_{12} = (k_{ii}\, k_{jj}\, K_{ij}\, f_{ij})^{½} \tag{2}$$

In this equation (2) K_{ii} is the equilibrium constant for the cross reaction, while f_{ij} may be calculated from the first three terms and is above 0.1 for all available data. According to (2), when the formal oxidation potential under the reaction conditions, E^{o}', and k_{ii} are known, the rate constant for all other reactions for which E^{o}', and k_{ii} are known may be calculated. Because the assumptions of adiabaticity and the barrier being the crossover point are incompatible, and electron transfer reactions are now known to be nonadiabatic, it is stated in reviews that the cross rate equation (2) is a naive assumption that cannot work well, because in the light of modern electron transfer theory, it should not. In collaboration with Jack Pladziewicz at University of Wisconsin-Eau Claire, we have shown that for a wide variety of couples including ferrocenes, amino and sulfur substituted alkenes and aromatic compounds, and hydrazine derivatives in acetonitrile at room temperature, (2) works well enough that measurement of a series of E^{o}' values and k_{12} values allows determination of a set of k_{ii} values that fits all the data for 164 reactions between 53 couples. The relative k_{ii} values are vary over a range of 10^{14}, as indicated below. We can determine k_{ii}(fit) values that are at or above diffusion control, as those for **TMTSF**, by studying reactions with extremely small k_{ii} hydrazines, because the k_{12} values actually measured are then well below diffusion control so they are not diffusion limited. The Eyring barriers derived from k_{ii}(fit), $\Delta G^{\ddagger}_{ii}$(fit), correlate rather well with calculated vibrational reorganization energy (λ_{vib}), which is clearly the most important factor affecting intrinsic reactivity. A requirement for a good correlation of $\Delta G^{\ddagger}_{ii}$(fit) with λ_{vib} is that both H_{ab} values and λ_{solv} must be rather similar for a wide variety of cross reactions. This has apparently not been predicted theoretically, but if it were not true, there would be more scatter than we see.



Although the k_{ii} fit values are the intrinsic reactivities, the value for H_{ab} must be known to evaluate the vertical reorganizational energy λ, and interpret the intrinsic reactivity in terms of electron transfer theory. Our data seem best correlated using the Levich and Dogodnoze (L&D) equation that like classical Marcus-Hush theory uses only H_{ab} and λ as electron transfer parameters but has the preexponential factor proportional to H_{ab}^2. Our reactions are clearly not all nonadiabatic, so we modified the L&D equation by replacing the λ/4 in the exponential factor by $\Delta G^* = \lambda/4 - H_{ab} + H_{ab}^2/\lambda$. (taken directly from two-state Marcus-Hush theory). Using this modified L&D equation different k_{ii}(fit) values produce parellel straight lines separated by $\Delta\Delta G^*$ in a ΔG^* versus log(H_{ab}) plot. H_{ab} for a given couple must be known to evaluate its ΔG^*. How to evaluate H_{ab} for intermolecular reactions has been a longstanding problem, but we argue that our data allow estimation of H_{ab} for some cases.

The unhindered planar π system compounds $\mathbf{TTF^{0/+}}$, $\mathbf{TMPD^{0/+}}$ and $\mathbf{DMP^{0/+}}$ can achieve best overlap of their π systems with a partner and should have the highest H_{ab} values for self-ET. Their ΔG^* values are in the same order and have similar spacing to their calculated $\lambda_{vib}/4$ values if their H_{ab} values are the same size, so we assume that they are about the same size. Their ΔG^* values agree with calculated λ_{vib} values if λ_{solv} is about 8 kcal/mol and H_{ab} is about 0.5 kcal/mol (170 cm^{-1}). H_{ab} cannot be very much less than 0.5 kcal/mole based on k_{ii}(fit) for our most reactive compound, $\mathbf{TMTSF^{0/+}}$. We cannot calculate its λ_{vib} because of its selenium atoms, but its λ_{vib} must be small because the solid doped with its radical cation becomes superconducting at low temperature. The total ΔG^* for $\mathbf{TMTSF^{0/+}}$ using H_{ab} = 0.5 kcal/mole is only about 2.2 kcal/mol, and this includes the solvent contribution, $\lambda_{solv}/4$. It is harder to establish an upper limit for H_{ab}, but if it were very much larger their rate constants would exceed the adiabatic limit, which we suggested would make their reactions not fit the cross rate equation because its basic assumption is that the reactions studied are activation barrier-limited.

Other conclusions from our work include: a) Dielectric continuum theory predictd λ_{solv} values that are larger and more sensitive to molecular size than fit experiment. b) H_{ab} for couples that cannot obtain direct overlap of their π systems (like saturated alkyl hydrazines with all alkyl groups ethyl and larger) are surprisingly constant, and on the order of 0.01 kcal/mol (3 cm^{-1}). c) Despite the small H_{ab}, none of the reactions studied appear to be nonadiabatic in the sense it is used by Jortner, because the modern nonadiabatic rate equation has e^{-S} in the preexponential term, and $S = \lambda_{vib}/h\nu_v$ varies so widely between aromatic compounds, ferrocenes, and hydrazines that which type of partner was used as the electron transfer partner would be important. Such an effect is not observed: only E^{o}' and k_{ii} are important in determining k_{12}, as stated in the simple, classical Marcus equation (2). d) λ_{vib} for ferrocenes has been substantially underestimated in the past.