

Physical Chemistry

Study of Free Energy Dependence of the Electronic Factor in Biological Long-Range Electron Transfer

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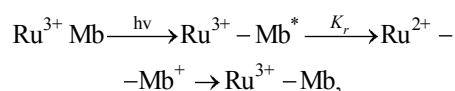
ABSTRACT. The donor and acceptor orbitals in long-range electron transfer are strongly exposed to environmental inertial polarization fluctuations. The most likely polarization at the moment of electron transfer is determined by the intersection region of two potential surfaces spanned by collective polarization coordinates and depends strongly on the temperature and reaction free energy. Those effects must therefore be reflected in corresponding variation of the electronic transmission coefficient with those quantities and not solely in the nuclear Franck-Condon factors. We estimated those effects for system parameters appropriate to intramolecular electron transfer in $(\text{NH}_3)_3\text{Ru}^{3+}$ and Zn^{2+} modified myoglobin. The estimates rest on vibrational calculation of a set of exponential trial wave functions in the instantaneous inertial polarization field and on a Hartree-Fock estimate of the distance decay of the Ru^{3+} and excited Zn orbitals involved. The effects are significant and dominated by a horizontal shift of the overall free energy relation by up to 0.5 eV toward numerically smaller values of the reaction free energy. This observation has important implications for electron tunnel distances in long-range electron transfer. © 2013 Bull. Georg. Natl. Acad. Sci.

Key words: modified myoglobin, long-range electron transfer, free energy dependence.

Electron transfer between molecular centers separated by distances that notably exceed the geometric extension of the molecular reactant groups is of great importance in several contexts. “Long-range” electron transfer of this kind is, for example, a key element in multisite red-ox proteins, in the electron-transfer sequences of photosynthesis and respiration, and in intramolecular chemical or biological electron-transfer systems, where the donor and acceptor groups are separated by molecular bridge groups.

In the present work we illustrate the effects that might be expected for long-range intramolecular elec-

tron transfer in modified metalloprotein systems. We refer specifically to $\text{Ru}(\text{NH}_3)_5^{2+}$ -modified sperm whale myoglobin as a suitable representative of this rapidly expanding area of electron transfer, as data for distance and reaction free energy variation have become available for this particular systems. The reactions are



where Mb^* represents excited state of the Mb heme

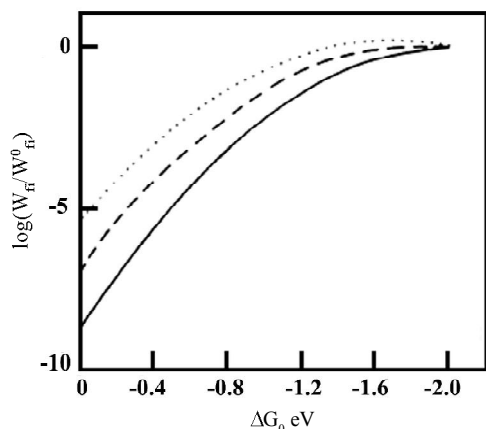


Fig. Calculated reaction free energy plots including modulation of the electronic factor and orbital decay parameters. W_{fi} is the transition probability per unit time obtained from (6) and W_{fi}^0 the transition probability per unit time in the absence of modulation, i.e. when the first term in the exponent on the right hand side of (6) vanishes. The preexponential factors in W_{fi} and W_{fi}^0 are cancelled in the ratio W_{fi}/W_{fi}^0 : (—) no electronic modulation; (---) electronic modulation included and 10 Å electron-transfer distance; (...) electronic modulation included and 20 Å electron-transfer distance.

or modified (Zn, Pb) heme group and k_r the electron transfer rate constant to be investigated. The distance variation is represented by Ru-modification at the His – 12, -48, -81 and -116 positions and the reaction free energy variation by modification with different Ru fragments or different metal substitution in the central meso-porphyrin IX group. In these ways the center-to-center electron-transfer distance can be changed from 12 to 22 Å and the reaction free energy from zero to 1 eV.

The reactions belong to the “normal” free energy range, i.e. $\theta^* > 0$, with a total reorganization free energy of about 2 eV. θ^* varies from 0.5 for $\Delta G \approx 0$ eV ($(\text{NH}_3)_5 \text{Ru}(48)\text{Mb Fe}$) to 0.25 for $\Delta G \approx 0$ eV ($(\text{NH}_3)_5 \text{Ru}(48)\text{Mb Fe}$).

The electron donor is an excited electronic state of the heme or modified heme group, giving a donor wave function at the ruthenium site. The coupling features are therefore dominated by the donor wave function.

The excited state delocalization can be illustrated by quantum chemical estimates of the decay prop-

erties of the electronic wave functions for to crude models of the donor and acceptor centers. We carried out Hartree-Fock calculations [1] for a Ru^{3+} ion. The split valence basis set was generated by splitting the outer valence shells in two parts with $N-1$ and a single primitive Gaussian type orbital, respectively. The basis set was (15s, 9p, 6d) – (6s, 4p, 3d) giving for the optimized highest filled Ru^{3+} orbital

$$\psi_{\text{Ru}^{3+}} = -0.32 d_{yz}^{(1)} + 0.82 d_{yz}^{(2)} + 0.34 d_{yz}^{(3)}, \quad (1)$$

where the dipole moments d are

$$d_{yz}^{(1)} = yz [0.128 e^{-7.377 \times 10^{-1} R^2} + 0.496 e^{-2.023 \times 10^{-1} R^2} + 0.580 e^{-6.184 R^2}], \quad (2)$$

$$d_{yz}^{(2)} = yz [0.234 e^{-2.823 R^2} + 0.559 e^{-9.3494 \times 10^{-1} R^2}],$$

$$d_{yz}^{(3)} = yz e^{-2.912 \times 10^{-1} R^2},$$

The $d_{yz}^{(3)}$ dominating amplitude would correspond to unscreened orbital exponents of $\lambda_{f0} \approx 5.5 \text{ \AA}^{-1}$, with

$$\begin{aligned} \psi_i &= (\lambda_i^3 / \pi)^{1/2} \exp(-\lambda_i | \vec{\rho} |); \quad \psi_f = \\ &= (\lambda_f^3 / \pi)^{1/2} \exp(-\lambda_f | \vec{\rho} - \vec{R} |) \end{aligned} \quad (3)$$

Here the $\vec{\rho}$ is the distance from the electron-transfer center, \vec{R} – the interreactant distance, and the only parameters are the orbital exponents λ_i and λ_f .

A similar calculation is less feasible for the donor center. The first excited state of Zn a atom for which we have carried out such a calculation gives an orbital exponent of 0.83 \AA^{-1} for $R = 2.65 \text{ \AA}$ and 1.7 \AA^{-1} for $R = 5.3 \text{ \AA}$, i.e. indeed substantially smaller than for Ru^{3+} . However, the excited Zn - porphyrin state corresponds to excitation in the porphyrin part rather than at the Zn atom.

Given calculations support the expectation that the excited state donor orbital decays significantly slower than the acceptor orbital. In view of the very crude representation of the electron-transfer center,

they cannot, of course, be viewed as a proper substantiation of this expectation.

When $\lambda_i \ll \lambda_f$, a simple form of the overlap integral emerges

$$S_{fi} = 8(\lambda_i / \lambda_f)^{3/2} \exp[-\lambda_i R^*]; \lambda_i = \lambda_i(\theta^*); \quad (4)$$

$$\lambda_f = \lambda_f(\theta^*).$$

In the following we assume that the variation of S_{fi} with θ^* or ΔG_0 and T essentially reflects the variation of the transition matrix elements V_{fi} . The electronic transmission coefficient \aleph_{fi} , then takes the approximate form:

$$\aleph_{fi} = \aleph_{fi}^{00} \exp[-2\lambda_{io}(1 - \xi\theta^*)R^*] \equiv$$

$$\equiv \aleph_{fi}^0 \exp(2\lambda_{io}\xi\theta^*R^*), \quad (5)$$

where \aleph_{fi}^{00} is the value of \aleph_{fi} at the minimum donor-acceptor distance, R_{\min} , while \aleph_{fi}^0 is the transmission coefficient at the initial – state equilibrium environmental nuclear configuration for given R^* . R^* coincides approximately with the intersite separation when $\lambda_i \ll \lambda_f$.

The experimental distance dependence data for electron transfer in modified myoglobins can be represented approximately by the exponential relation $[-0.9(R - R_{\min})]$ (R in angstroms). By eq. (4) it gives $\lambda_{i0} \approx 0.6 \text{ \AA}^{-1}$ for the donor orbital exponent equilibrated with the environmental polarization. This value is in line with estimates for several strongly exothermic, activationless processes where the electron-transfer configuration is that of initial state equilibrium.

The variation of the nuclear factor with θ^* in the transition probability $W_{fi}(\theta^*)$ is, from electron-transfer theory [2], $W_{fi} \propto \exp(-\beta E_s \theta^{*2})$; $\beta = (k_B T)^{-1}$. By including the electronic modulation in eq. (4), the overall variation of $W_{fi}(\theta^*)$ with θ^* becomes in the

high-temperature limit

$$W_{fi}(\theta^*) \propto \exp[2\lambda_{i0} \xi \theta^* R^* - \beta E_s \theta^{*2}] \quad (6)$$

this equation has two implications:

$W_{fi}(\theta^*)$ assumes its maximum value for , i.e. for $\theta^* = \theta_m^* = (\xi / \beta E_s) \lambda_{i0} R^*$ positive θ^* or $\Delta G_0 | < E_s$.

If modulation is disregarded, $W_{fi}(\theta^*)$ has maximum for $\theta^* = 0$, or $\Delta G = -E_s$. For $\xi = 5/11$, $T = 298 \text{ K}$ and $E_s = 2 \text{ eV}$; θ_m^* is 0.034 and 0.068 when $\lambda_{i0} R^* = 6 (R = 10 \text{ \AA})$ and $12 (R = 20 \text{ \AA})$, respectively.

This corresponds to shifts in the $W_{fi}(\theta^*)$ maximum of 0.14 and 0.28 eV, respectively. The shift is smaller at lower temperatures when nuclear tunneling in the solvent vibrational spectrum is important [3].

Inclusion of the modulation effects also shifts the whole free energy plot horizontally toward lower values without significant changes of its shape. For the data in [4] ($R = 12 \text{ \AA}$), the shift would amount to 0.15 – 0.20 eV but it would be expected to be larger for free energy relations based on substitution at more remote sites from the heme group.

Free energy relations based on modification at different histidines might offer a new perspective also for illumination of environmental modulation of the electronic factor in electron-transfer theory. At the same time the continuum formalism used [5], which can be extended to solvent structural effects in the form of vibrational and spatial dielectric dispersion, is a useful frame for incorporation of large numbers of solvent molecules and nonequilibrium solvation effects for which quantum chemical approaches are not feasible. On the basis of this formalism, a family of almost parallel free energy plots would be expected when the fragments are attached to different His sites. Those plots are shifted to decrease reaction free energies with increasing electron-transfer distance, and the equilibrium values of the electronic parameters can be extracted from the shifts.

ფიზიკური ქიმია

ბიოლოგიურ სისტემებში შორ მანძილებზე ელექტრონის გადატანისას ელექტრონული ფაქტორის თავისუფალ ენერგიაზე დამოკიდებულების შესწავლა

მ. ზაქარაია

ი. ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტის რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი

(წარმოდგენილია აკადემიკოს გ. ცინცაძის მიერ)

შორ მანძილებზე ელექტრონის გადატანისას დონორისა და აქცეპტორის ორბიტალები მნიშვნელოვნად არიან დამოკიდებული გარემოს ინერციული პოლარიზაციის ფლუქტუაციებზე. ელექტრონის გადასვლის მომენტში პოლარიზაცია ორი პოტენციალური ზედაპირის გადაკვეთით განისაზღვრება და ძლიერად არის დამოკიდებული ტემპერატურისა და რეაქციის თავისუფალ ენერგიაზე. ეს ეფექტები უნდა აისახებოდეს ელექტრონის ტრანსმისიური კოეფიციენტის ვარიაციებში და არა მხოლოდ ფრანკ-კონდონის ბირთვულ ფაქტორებში. ეს ეფექტები ჩვენ განვიხილეთ $(\text{NH}_3)_3\text{Ru}^{3+}$ და Zn^{2+} მოდიფიცირებულ მთვლიანობაში ელექტრონის გადატანის პარამეტრებისათვის. ჩვენი დაშვებანი ეფუძნება მყისიერ ინერციულ პოლარიზაციულ ველსა და ჰარტრი-ფოკის დაშვებით Zn აგზნებულ ორბიტალებზე საცდელი, ექსპონენციალური ტალღური ფუნქციების ვარიაციულ გამოთვლებს. ეფექტები საგრძობია და დომინირებენ თავისუფალი ენერგიის ცვლილებისას 0.5 eV -დან ნაკლებ მნიშვნელობამდე. მოცემულ სამუშაოში წარმოდგენილი მოსაზრებები მნიშვნელოვანია ელექტრონის ტუნელირების მანძილის განსაზღვრისათვის ელექტრონის შორ მანძილებზე გადატანისას.

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Received October, 2013