

The Effects of Local Heating of Proteins in Electron Transfer

V.D. Lakhno* and L.A. Uvarova**

* Institute of Mathematical Problems of Biology, Russian Academy of Sciences, Pushchino
Tver' State University, Tver', Russia

Abstract - It is found that local heating of proteins in the electron transfer zone can significantly affect the rate of the transfer reaction. When an electron is transferred over 5 to 6Å, local heating can reach tens of degrees, resulting in temperature dependence of the reaction rate at helium temperatures.

The problem of electron transfer over a large distance is one of the most important questions in molecular biology. It is significant that, in many cases, this transfer proceeds via the tunneling mechanism. The temperature dependence of the transfer rate is governed mainly by tunneling across the nuclear subsystem of the biomacromolecule. Electron transfer is usually accompanied by large heat liberation. Thus, at a photo reactive site in photosynthesis, heat is liberated in the electron-transport chain during electron transfer from bacteriochlorophyll to quinone. Exchange reactions of proteins in aqueous solutions are also often accompanied by the liberation of heat. Here, it is important that the expressions for calculating the electron-transfer rate contain the average equilibrium temperature of the medium T_0 [1,2]. At the same time, it is quite obvious that heat released in the region of electron transfer to a localized state produces a local heating of the immediate nuclear surroundings. In this work, we investigated the effect of local heating of the medium on the electron transfer rate.

In considering the local heating process, we used two macro-models that describe heat transfer in a three-layer globule. The simplest three-layer-globule model used for description of electron processes in proteins [3, 4] is shown in Fig. 1.

Model 1. This model assumes that a small part of the immediate surroundings of the site where the electron is localized is heated to a temperature T^* either during the electron transfer process or due to relaxation of a photo excited electron. Generally, this heating occurs within a very short time (about a femtosecond) with subsequent transfer of the heat to the degrees of freedom of the surrounding medium. In hem-containing proteins, the inner region is determined by the size of the hem, and as an estimate, we assume that its radius equals $R_1 \sim 3-5$ Å. A typical value of the outer radius is $R_2 \sim 10-20$ Å.

We will use the macroscopic approximation for a macromolecule. This approximation makes it possible to obtain an analytical solution of the problem, and as a macromolecule contains $\sim 500-1000$ atoms, this approximation is applicable. Thus, for instance, Tesch and Schulten studied cooling a sphere of radius $R \sim 30$ Å (a model of a two-layer globule) using both the molecular dynamics method and the heat-conduction equation [5]. A comparison shows that the average temperatures found by these methods are nearly identical.

The heat conduction equations for the first and second zones assume the form:

$$\frac{\partial T_1}{\partial t} = a_1(\bar{T}_1) \left(\frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right), \quad 0 \leq r < R_1, \quad (1)$$

$$\frac{\partial T_2}{\partial t} = a_2(\bar{T}_2) \left(\frac{\partial^2 T_2}{\partial r^2} + \frac{2}{r} \frac{\partial T_2}{\partial r} \right), \quad R_1 < r < R_2. \quad (2)$$

The initial conditions and boundary conditions for (1) and (2) that correspond to the assumptions in the model are

$$T_1(0, t) < \infty, \quad T_1(r, 0) = T^*, \quad T_2(r, 0) = T_0, \quad T_2(R_2, t) = T_0, \quad T_1(R_1, t) = T_2(R_1, t),$$
$$-\chi_1(T_1) \left. \frac{\partial T_1}{\partial r} \right|_{R_1, t} = -\chi_2(T_2) \left. \frac{\partial T_2}{\partial r} \right|_{R_1, t} \quad (3)$$

Here, α_i , χ_i , (where $i=1,2$) denote the thermal diffusivity ($\alpha_i=\chi_i / C_{pi} \rho$) and the heat conductivity, respectively; C_{pi} denotes the heat capacity and ρ_i , is the density. In general, all the thermo-physical characteristics vary with temperature [6], and the boundary-value problem (1)-(3) must be solved by the grid method using formulas of continuous computations. In this work, we considered the dependence of the thermal diffusivity on the temperature averaged over the volume of the zone, \bar{T}_i . We also assumed that the character of the $\alpha_i(T_i)$ dependence is the same in zones 1 and 2, i.e., that $\alpha_i = \alpha_i(T_0) \gamma(T_i)$ and, similarly, that $\chi_i = \chi_i(T_0) \delta(T_i)$. With the assumptions made above, an analytical solution of the problem can be obtained by employing the operational method. Inasmuch as the solution for zone 1 is only needed to determine the interface temperature $T_1(R_1, t) = T_2(R_1, t)$, in the following, we only give the solution for zone 2:

$$T_2 = T_0 + \frac{2(T^* - T_0)R_1}{r} \kappa \times \sum_{n=1}^{\infty} \frac{\varphi_n \sin(y_n(d-x)) \exp(-y_n^2 \tau)}{\sin(y_n(d-1))}, \quad (4)$$

where

$$\varphi_n = (1 - b y_n \cot b y_n) \times \left(1 - \kappa + \frac{\kappa b^2 y_n^2}{\sin^2 b y_n} + \frac{y_n^2 (d-1)}{\sin^2 (d-1) y_n} \right)^{-1}.$$

Here, we used the following notations:

$$\begin{aligned} \kappa &= \chi_1(T_0) \chi_2^{-1}(T_0), & x &= \frac{r}{R_1}, & d &= \frac{R_2}{R_1}, \\ b &= \left(\frac{a_2(T_0)}{a_1(T_0)} \right)^{0.5}, & \tau &= \frac{1}{t_\infty} \int_0^t \gamma(\bar{T}_2(t)) dt, & t_\infty &= \frac{R_1^2}{a_2(T_0)}. \end{aligned}$$

The value of y_n is given by the equation

$$1 - \kappa + \kappa b y \cot b y + y \cot y (d-1) = 0. \quad (5)$$

If $\kappa \sim 1$, from (5) it follows that $y_n = \pi n/d$. The average temperature,

$$\bar{T}_2(t) = T_0 + \frac{4\pi}{(4/3)\pi(R_2^3 - R_1^3)} \int_{R_1}^{R_2} (T_2 - T_0) r^2 dr, \quad (6)$$

is found from the expressions

$$\bar{T}_2(\tau) = T_0 + \frac{6(T^* - T_0)}{d^3 - 1} \sum_{n=1}^{\infty} \delta_n \exp(-y_n^2 \tau), \quad (7)$$

$$t = t_\infty \int_0^\tau \frac{d \zeta}{\gamma(\bar{T}_2(\zeta))}, \quad (8)$$

where

$$\delta_n = \frac{\varphi_n}{y_n} \left\{ d [\sin y_n (d-1)]^{-1} - \frac{\kappa}{y_n} (1 - b y_n \cot b y_n) \right\}.$$

For $\gamma(\bar{T}_2) = 1$, the average temperature is given by

$$\bar{T}_2(t) = T_0 + \frac{6(T^* - T_0)}{d^3 - 1} \sum_{n=1}^{\infty} \delta_n \exp(-y_n^2 t t_{\infty}^{-1}). \quad (9)$$

Equation (9) can also be used as a first approximation, for subsequent correction of the $\tau(t)$ dependence at

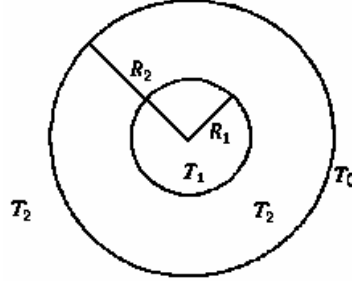


Fig. 1. Spherical, symmetrical model of a three-layer globule.

variable $\gamma(\bar{T}_2)$ and, correspondingly, for refining the $\bar{T}_2(t)$ value.

When $b/(d-1)$ can be represented as a ratio of two natural numbers, the following sum must be added to the solution (4):

$$S_2 = \frac{-2(T^* - T_0)R_1\kappa b}{\pi n_0 r \beta} \times \sum_{j=1}^{\infty} \sin(\pi \mu_j (x-1)) j^{-1} \exp(-\mu^2 j^2 \tau),$$

where $n = n_0 j$, n_0 is the smallest of the natural numbers n for the $b/(d-1)=n/m$ ratio mentioned, $\mu = \pi n_0/b$, and $\beta = \kappa(d-1) + 1$. Correspondingly, the following sum will be added to the right-hand side of (6):

$$\bar{S}_2 = \frac{6(T^* - T_0)\kappa b^2}{\pi^3 n_0^3 \beta (d^3 - 1)} \sum_{j=1}^{\infty} j^{-2} ((-1)^m - 1) \exp(-\mu^2 j^2 \tau).$$

Model 2. Model 2 is a modified version of Model 1. The heating kinetics can be described without assigning the temperature value T^* if we introduce a source $qf(t)$ into the right-hand side of (1):

$$\frac{\partial T_1}{\partial t} = a_1(\bar{T}_1) \left(\frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right) + \frac{qf(t)}{C_{p1} \rho_1}. \quad (1')$$

The magnitude of q can be estimated from the condition $q = h\nu/V_0 t_0$, where ν is the light frequency in the absorption band, V_0 is the volume of a region of radius R_1 , and $t_0 \sim \nu^{-1}$. Function $f(t)$ depends strongly on the duration of the action of the source, i.e., on time t_0 . It can be written in the form of the step function:

$$f(t) = \begin{cases} 1, & t \leq t_0 \\ 0, & t > t_0 \end{cases}. \quad (10)$$

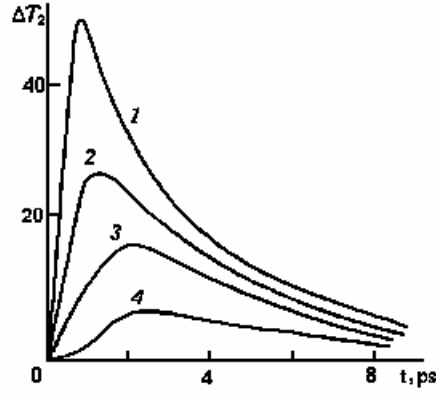


Fig. 2. The $\Delta T_2(r, t)$ dependences for various values of radial variable r (Model 1): (1) 6, (2) 7.5, (3) 9, (4) 12 Å.

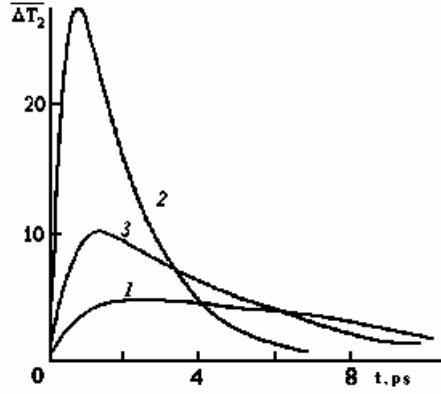


Fig. 3. Average overheating at various values of the outer radius R_2 : (1) 15, (2) 10, (5) 20 Å.

The solution for temperature T_2 , as found from (1')-(3) and (10), is

$$T_2 = T_0 + \frac{2\kappa q R_1 t_\infty}{C_{p1}(T_0)\rho_1(T_0)r} \times \sum_{n=1}^{\infty} \frac{\sin(y_n(d-x))\varphi_n \psi_n(t)}{y_n^2 \sin(y_n(d-1))}, \quad (11)$$

where

$$\psi_n(t) = \begin{cases} \psi_n^{(1)}(t) = 1 - \exp(-y_n^2 t t_\infty^{-1}), & t \leq t_0 \\ \psi_n^{(2)}(\Delta \tau) = \psi_n^{(1)}(t_0) \exp(-y_n^2 \Delta \tau), & t > t_0, \end{cases}$$

$$\Delta \tau = t_\infty^{-1} \int_{t_0}^t \gamma(\bar{T}_2(\zeta)) d\zeta.$$

Here, at $t \leq t_0$, the problem was solved for constant values of C_p , ρ , and a because of the small t_0 value compared with the relaxation time t_∞ . The average temperature $\bar{T}_2(t > t_0)$ is found from (8) [in which t must be replaced by $(t - t_0)$ and τ by $\Delta \tau$] and the following equation:

$$\bar{T}_2(\Delta \tau) = T_0 + \frac{6\kappa q t_\infty}{C_{p1}(T_0)\rho_1(T_0)(d^3 - 1)} \times \sum_{n=1}^{\infty} \frac{\delta_n}{y_n^2} \psi_n^{(2)}(\Delta \tau). \quad (12)$$

At $\gamma_2(\bar{T}_2)=1$, we have, in particular, $\Delta\tau = (t - t_0)t_\infty^{-1}$. If $b/(d - 1) = n/m$, the following sum must be added to the right-hand side of (11):

$$\sigma_2 = \frac{-2q\kappa b^3 t_\infty R_1}{C_{p1}(T_0)\rho_1(T_0)\pi^3 r n_0 \beta} \times \sum_{j=1}^{\infty} \sin(\nu_j(x-1))j^{-3}\alpha_j(t),$$

where

$$\alpha_j(t) = \begin{cases} \alpha_j^{(1)}(t) = 1 - \exp(-\nu^2 j^2 t t_\infty^{-1}), & t \leq t_0 \\ \alpha_j^{(2)}(\Delta\tau) = \alpha_j^{(1)}(t_0) \exp(-\nu^2 j^2 \Delta\tau), & t > t_0. \end{cases}$$

A corresponding sum found from σ_2 and (6) is added to the right-hand side of (12).

The results of calculations carried out using these solutions are presented in Figs. 2-5. In calculations, it was assumed that $C_{p1} \sim C_{p2} \sim 1.2 \times 10^3$ J/(kg K) (this value is consistent with the heat capacity of proteins at $T = 300$ K [7]), $a_1 \sim a_2 \sim 7 \times 10^{-8}$ m²/s [5], $\rho_1 \sim \rho_2 \sim 10^3$ kg/m³, and, respectively, $x_1 \sim x_2 \sim 0.1$ J/(m s K). Temperature T^* was estimated with the following considerations: Typical energies associated with electron transfer range from one to two eV. Assuming that the energy of an absorbed photon is distributed among the N degrees of freedom of a heme group with $N = 3N_a - 6$ [8] (N_a is the number of atoms in the heme group - $N_a = 20-40$) and using the relation $h\nu = kN(T^* - T_0)/2$, for a wavelength $\lambda = 530$ nm, we find that the overheating ($T^* - T_0$) can be $\sim 500 - 1000$ K. In the calculations, we also assumed that $R_1 = 3.5$ Å, $R_2 = 15$ Å (Figs. 2, 4), and $N_a = 24$.

Calculations for the macroscopic models show marked local overheating caused by electron transfer in biomacromolecules ($\sim 100-200$ K at $\Delta r \sim 1$ Å, and of the order of tens of degrees at $\Delta r \sim 5$ to 6 Å, where $\Delta r = r - R_1$ is the distance from the heme region). The values of the maximum overheating averaged over the volume, $(\overline{\Delta T_2})_{\max}$, were 10-20 K (depending on the magnitude of R_2 and the model used). This is consistent with the results of Henry et al. [8], in which heating of macromolecules during photo-excitation was investigated by the molecular dynamics method. The calculations indicate also that the local temperature rise can significantly affect electron transfer for reaction times $t \leq 3-5$ ps. Intraglobular electron transfer that proceeds immediately after electron relaxation on the donor is such a reaction.

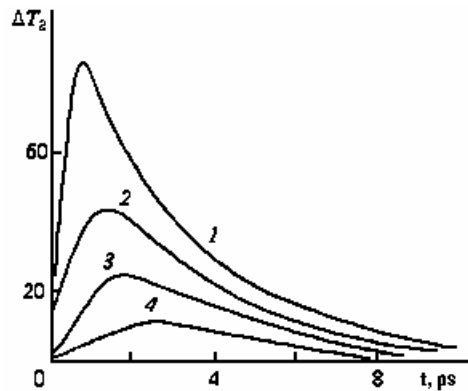


Fig. 4. The $\Delta T_2(t)$ dependences for various values of radius r (Model 2): (1) 6, (2) 7.5, (3) 9, (4) 12 Å.

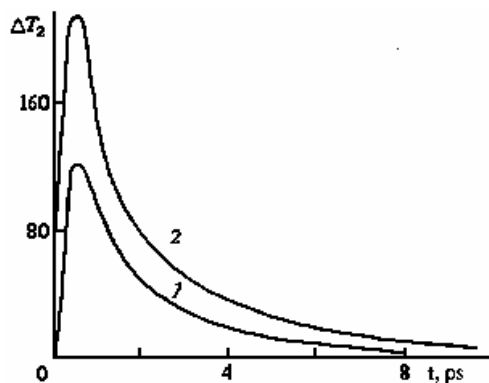


Fig. 5. ΔT_2 as a function of time at $r=4.5 \text{ \AA}$: (1) Model 1, (2) Model 2.

The temperature rise should also be taken into account in evaluating the rates of reactions involving electrons that occur immediately after the electron relaxation caused by photoexcitation. The temperature, at which the temperature-independent reaction mode is replaced by the activation mode, is about 100 K for a tunneling reaction. The importance of allowing for the heating phenomenon investigated in this work follows from the fact that the dependence of the electron transfer rate at low temperatures on activation is determined precisely by the nuclear subsystem of the zone in which the electron transfer occurs. Thus, if the distance between the donor and the acceptor is $\sim 4.5 \text{ \AA}$ and the reaction time is $t \sim 2 \text{ ps}$, the character of the transfer will be of the activation type (in Model 2), even at an equilibrium temperature of the medium of $T_0 \sim 20 \text{ K}$, because local heating under these conditions is $\sim 80 \text{ K}$. Model 1 yields a similar result at $t \sim 1 \text{ ps}$.

The solutions also reveal that, for a diminishing $\gamma(T)$ function, temperature T_2 will attain the equilibrium value T_0 more slowly than at constant thermo-physical characteristics.

Allowance for the effects of anisotropy of the macroscopic biomacromolecule characteristics, as well as of nonlinearity of the macromolecular properties in future calculations proves to be interesting. The fundamentally important effects caused by this type of non-linearity may include a delay in propagation of the heat packet and other peculiarities.

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