6. Y. Kimura *et al.*, *Nature* **389**, 206 (1997); N. Grigorieff, T. A. Ceska, K. H. Downing, J. M. Baldwin, R. Henderson, *J. Mol. Biol.* **259**, 393 (1996).
7. E. Pebay-Peyroula, G. Rummel, J. P. Rosenbusch, E. M. Landau, *Science* **277**, 1676 (1997).
8. L. Song, M. A. El-Sayed, J. K. Lanyi, *ibid.* **261**, 891 (1993).
9. S. L. Logunov, L. Song, M. A. Elsayed, *J. Phys. Chem.* **100**, 18586 (1996).
10. Q. Zhong *et al.*, *J. Am. Chem. Soc.* **118**, 12828 (1996).
11. J. K. Delaney *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **92**, 2101 (1995); J. K. Delaney *et al.*, *J. Phys. Chem.* **97**, 12416 (1993).
12. R. W. Schoenlein *et al.*, *Science* **254**, 412 (1991); T. Kobayashi *et al.*, *J. Phys. Chem. B* **102**, 272 (1998); H. Kandori *et al.*, *Chem. Phys. Lett.* **211**, 385 (1993); T. Arlt, S. Schmidt, W. Zinth, U. Haupts, D. Oesterhelt, *ibid.* **241**, 559 (1995).
13. D. Oesterhelt and W. Stoeckenius, *Nature New Biol.* **233**, 149 (1971).
14. E. Racker and W. Stoeckenius, *J. Biol. Chem.* **249**, 662 (1974).
15. Retinal also functions as the visual pigment in rhodopsin, where it photoisomerizes from its 11-*cis* form to its all-*trans* form and triggers a visual response.
16. A. Lewis *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **71**, 4462 (1974); N. V. Katre *et al.*, *ibid.* **78**, 4068 (1981).
17. M. Braiman and R. A. Mathies, *ibid.* **79**, 403 (1982); M. J. Pettei *et al.*, *Biochemistry* **16**, 1955 (1977); S. O. Smith *et al.*, *J. Membr. Biol.* **85**, 95 (1985); S. O. Smith *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **83**, 967 (1986).
18. K. Gerwert, B. Hess, J. Soppa, D. Oesterhelt, *Proc. Natl. Acad. Sci. U.S.A.* **86**, 4943 (1989); M. S. Braiman *et al.*, *Biochemistry* **27**, 8516 (1988).
19. Y. Koyama *et al.*, *Photochem. Photobiol.* **54**, 433 (1991).
20. M. G. Motto, M. Sheves, K. Tsujimoto, V. Balogh-Nair, K. Nakanishi, *J. Am. Chem. Soc.* **102**, 7947 (1980); K. Nakanishi *et al.*, *ibid.*, p. 7945.
21. R. Govindjee *et al.*, *Biophys. J.* **58**, 597 (1990); M. Rohr *et al.*, *J. Phys. Chem.* **96**, 6055 (1992); L. Song *et al.*, *ibid.* **100**, 10479 (1996).
22. M. A. Elsayed and S. Logunov, *Pure Appl. Chem.* **69**, 749 (1997).
23. J. K. Lanyi, *J. Biol. Chem.* **272**, 31209 (1997).
24. R. R. Birge *et al.*, *J. Am. Chem. Soc.* **113**, 4327 (1991).
25. S. L. Logunov and M. A. Elsayed, *J. Phys. Chem. B* **101**, 6629 (1997).
26. G. Varo and J. K. Lanyi, *Biochemistry* **30**, 7165 (1991).
27. The 13-*cis* form is destabilized in "light-adapted" bR, where the C=N bond of the Schiff base is maintained in the *anti* configuration; it becomes nearly as stable as all-*trans* retinal when the C=N bond "isomerizes" to its *syn* configuration. Both the all-*trans* with *anti* and the 13-*cis* with *syn* forms are populated in "dark-adapted" bR. See G. S. Harbison *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **81**, 1706 (1984).
28. K. J. Kaufmann, P. M. Rentzepis, W. Stoeckenius, A. Lewis, *Biochem. Biophys. Res. Commun.* **68**, 1109 (1976).
29. T. Althaus, W. Eisfeld, R. Lohrmann, M. Stockburger, *Isr. J. Chem.* **35**, 227 (1995); H. Hamaguchi and T. L. Gustafson, *Annu. Rev. Phys. Chem.* **45**, 593 (1994); T. L. Brack and G. H. Atkinson, *J. Phys. Chem.* **95**, 2351 (1991); S. J. Doig, P. J. Reid, R. A. Mathies, *J. Chem. Phys.* **85**, 6372 (1991); G. H. Atkinson *et al.*, *Chem. Phys.* **131**, 1 (1989).
30. J. W. Petrich *et al.*, *Chem. Phys. Lett.* **137**, 369 (1987).
31. R. A. Mathies *et al.*, *Science* **240**, 777 (1988).
32. J. Dobler, W. Zinth, W. Kaiser, D. Oesterhelt, *Chem. Phys. Lett.* **144**, 215 (1988).
33. R. R. Alfano *et al.*, *Biophys. J.* **16**, 541 (1976); S. L. Shapiro *et al.*, *ibid.* **23**, 383 (1978).
34. S. L. Dexheimer *et al.*, *Chem. Phys. Lett.* **188**, 61 (1992).
35. K. C. Hasson, F. Gai, P. A. Anfinrud, *Proc. Natl. Acad. Sci. U.S.A.* **93**, 15124 (1996).
36. F. Gai, K. C. Hasson, P. A. Anfinrud, in *Ultrafast Phenomena X*, P. F. Barbara, J. G. Fujimoto, W. H. Knox, W. Zinth, Eds. (Springer Ser. Chem. Phys. 62, Springer-Verlag, Berlin, 1996), pp. 353–354.
37. G. Haran *et al.*, *Chem. Phys. Lett.* **261**, 389 (1996).
38. F. Gai, J. C. McDonald, P. A. Anfinrud, *J. Am. Chem. Soc.* **119**, 6201 (1997).
39. K. Schulten *et al.*, *Isr. J. Chem.* **35**, 447 (1995); W. Humphrey, E. Bamberg, K. Schulten, *Biophys. J.* **72**, 1347 (1997); J. R. Tallent, J. A. Stuart, Q. W. Song, R. R. Birge, in preparation.
40. G. G. Kochendoerfer and R. A. Mathies, *Isr. J. Chem.* **35**, 211 (1995).
41. K. F. Freed, in *Radiationless Processes in Molecules and Condensed Phases*, F. K. Fong, Ed. (Springer, Berlin, 1976), pp. 23–168.
42. L. D. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932); C. Zener, *Proc. R. Soc. London Ser. A* **137**, 696 (1932).
43. S. L. Logunov, M. A. El-Sayed, J. K. Lanyi, *Biophys. J.* **70**, 2875 (1996).
44. S. L. Logunov, M. A. El-Sayed, L. Song, *J. Phys. Chem.* **100**, 2391 (1996).
45. M. Du and G. R. Fleming, *Biophys. Chem.* **48**, 101 (1993).
46. D. Beece *et al.*, *Biochemistry* **19**, 5147 (1980).
47. S. F. Gull and G. J. Daniell, *Nature* **272**, 686 (1978); P. J. Steinbach *et al.*, *Biophys. J.* **61**, 235 (1992).
48. Multiexponent kinetics are not unique to bR: the chemical dynamics of halorhodopsin (hR) have also been modeled with two to three exponential components [H. Kandori, K. Yoshihara, H. Tomioka, H. Sasabe, Y. Shichida, *Chem. Phys. Lett.* **211**, 385 (1993); T. Arlt, S. Schmidt, W. Zinth, U. Haupts, D. Oesterhelt, *ibid.* **241**, 559 (1995)], although it remains to be determined whether the hR kinetics are distributed or arise from two (or more) well-defined components.
49. F. Gai, K. C. Hasson, J. C. McDonald, P. A. Anfinrud, unpublished data.
50. Experimental methods: The pump pulse was generated by frequency doubling the signal output of a home-built β-barium borate–based optical parametric amplifier (OPA). The probe pulse was derived from a broadband continuum that was generated by focusing the output of a second OPA into a 3-mm sapphire crystal. A regeneratively amplified Ti:sapphire laser system (Clark-MXR, Dexter, MI) generated the optical pulses (1 kHz, 0.8 mJ, 120 fs, 780 nm) that powered the two OPAs. The bR sample (Sigma) was suspended in Hepes buffer (pH 7.4) and loaded into a sample cell with a 1-mm path length.

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Electron Transfer: Classical Approaches and New Frontiers

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Electron transfer, under conditions of weak interaction and a medium acting as a passive thermal bath, is very well understood. When electron transfer is accompanied by transient chemical bonding, such as in interfacial coordination electrochemical mechanisms, strong interaction and molecular selectivity are involved. These mechanisms, which take advantage of "passive self-organization," cannot yet be properly described theoretically, but they show substantial experimental promise for energy conversion and catalysis. The biggest challenge for the future, however, may be dynamic, self-organized electron transfer. As with other energy fluxes, a suitable positive feedback mechanism, through an active molecular environment, can lead to a (transient) decrease of entropy equivalent to an increase of molecular electronic order for the activated complex. A resulting substantial increase in the rate of electron transfer and the possibility of cooperative transfer of several electrons (without intermediates) can be deduced from phenomenological theory. The need to extend our present knowledge may be derived from the observation that chemical syntheses and fuel utilization in industry typically require high temperatures (where catalysis is less relevant), whereas corresponding processes in biological systems are catalyzed at environmental conditions. This article therefore focuses on interfacial or membrane-bound electron transfer and investigates an aspect that nature has developed to a high degree of perfection: self-organization.

Electron transfer, especially as an interfacial reaction, is a tremendously important process that controls mechanisms ranging from photosynthesis and respiration to electrochemical energy systems and corrosion. Understanding of its principles began basically in the 1940s with the transition state theory (TST) (*1*) and the Kramers theory (*2*) describing reaction rates on a microscopic basis. According to the Kramers theory, the rate constant accounts for the "frictional" effect of the surrounding medium, the immediate chemical surrounding of the electron transfer species, and includes the TST result as an upper limit. A largely empirical concept for understanding the dependence of rate constants on thermodynamic and molecular dynamic parameters was developed in the 1950s with a subsequent justification by derivation from basic principles (*3*). For this accomplishment,

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Marcus was awarded the Nobel Prize. In the principal formula involved, the rate of electron transfer k is related to the Gibbs free energy difference between electron donor and acceptor, ΔG°, and the reorganization energy λ, that is, the energy required for thermal reorganization of the molecular environment to permit isoenergetic electron exchange. This formula was limited primarily to weak interaction, that is, to a small overlap of the electronic orbitals. Vibrational and collision parameters, as well as intervening molecular structures, are additionally considered and add varying degrees of sophistication to the electron transfer model (*4*).

Passive Medium, Weak Interaction

In spite of being theoretically limited to weak interaction and to quasi-equilibrium statistical processes, the Marcus formula has been applied successfully to many problems of electron transfer, both in chemistry and biology:

$$k = A \exp(-\Delta G^*/k_B T) \qquad (1)$$

$$\Delta G^* = w + (\Delta G^\circ + w_p - w + \lambda)^2/4\lambda \qquad (2)$$

$$\lambda = \lambda_o + \lambda_i \qquad (3)$$

where A is a preexponential factor, ΔG^* is the Gibbs free energy of activation, k_B is the Boltzmann constant, T is temperature, ΔG^0 is the Gibbs free energy of the elementary electron transfer step, which is $-e\eta$ for the electrode case (η is the corresponding electrical potential), λ_o and λ_i are the solvent reorganization energies for the outer and the inner sphere, respectively, w is the work needed to bring the two reactants, or the reactant and the electrode, together, and w_p is the corresponding term for the products.

More sophisticated models have also been used for electron transfer in complex biomolecular systems. For example, the superexchange theory has been applied successfully to a variety of systems (*5*). Electrochemistry has also drawn substantial advantages from these concepts, especially since Gerischer matched them with solid state quantum mechanical schemes to describe isoenergetic electron exchange between energy bands in solids and in redox systems in solution (*6*). In all of these cases, electron transfer can be inverted. The medium plays only a passive role, acting as a thermal bath. It provides the Boltzmann-distributed polarizational fluctuations needed for the preparation of states before the isoenergetic electron exchange. In the 1980s, the frictional effect of the fluctuating medium in analogy to the Kramers theory was introduced by Zusman and elaborated by Sumi and Marcus (*7*). However, in all of these theories, the specific chemistry of the species involved is considered only through thermodynamic and statistical parameters. This limits the applicability of the theory, in spite of its great success, and raises the question of what thermal statistics mean when electron transfer processes can be as fast as 20 fs (*8*).

Passive Self-Organization, Strong Interaction

Many systems for energy conversion and catalysis, ranging from photoelectrolysis of water to oxygen reduction in fuel cells and nitrogen fixation, involve multielectron transfer or selective interactions. Such mechanisms occur under conditions of strong molecular interaction, which is needed to bind intermediates to achieve an overall favorable electrochemical potential of the total reaction. It cannot be easily described theoretically because the complicated quantum mechanical interaction would have to be considered. Work on "inner sphere" electron transfer has provided a good basis for qualitative understanding (*9*) although it does not yet adequately consider the dynamics of structural order generated during coordinative electron transfer processes.

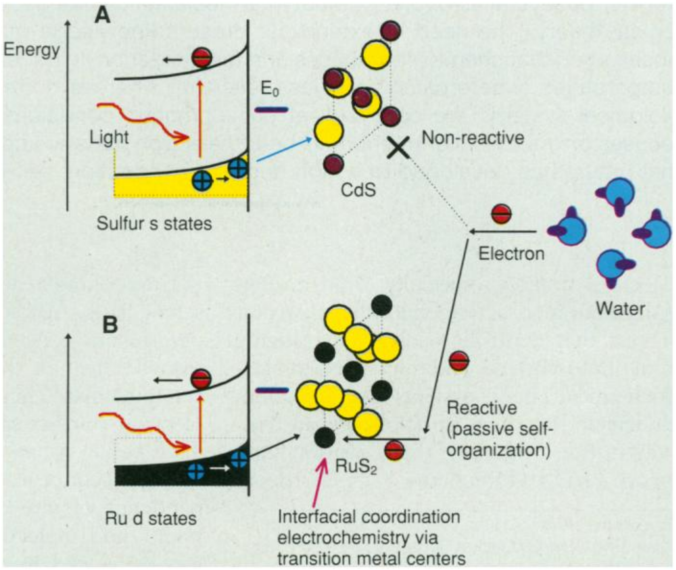

Fig. 1. Energy schemes showing energy bands and the simplified molecular interface with water of the photoactive semiconductors cadmium sulfide (**A**) and ruthenium disulfide (**B**), where E_0 denotes the standard electrochemical potential of the redox reaction H_2O/O_2. In spite of satisfied thermodynamic conditions, electron transfer (visualized in the figure) may be either suppressed or very efficient as a consequence of passive self-organization of reactants at transition metal centers, as shown for the photooxidation of water to molecular oxygen at ruthenium disulfide compared with the nonreactive cadmium sulfide (which does not accept electrons from water).

The Marcus formula and the quantum mechanical intuitive Gerischer approach for interfaces predict identical reactivities for electrons reacting from given electron levels irrespective of the nature of electronic states involved (polar bonding, nonbonding transition metal d state, and sulfur s state), provided that the considered parameters (ΔG° and λ) and the solvent conditions are comparable. Much electrochemical experimental data show that this is an idealized situation and that the surrounding medium has a crucial effect on interfacial electron transfer. In fact, depending on the chemistry involved in electron transfer, passive self-organization of the medium can be applied for more efficient electron transfer: For example, electrons of water show no reactivity with vacant electronic states (sulfur s states) in the valence band of the illuminated semiconductor CdS, even though it would be thermodynamically possible (Fig. 1A).

If, on the other hand, the vacant state is generated in the valence band of illuminated RuS_2, which is a Ru d state, oxidation of water will readily occur with a quantum efficiency for oxygen evolution of 70% (Fig. 1B). The key difference is that a missing s state electron is equivalent to a missing polar bond, whereas a missing d state electron increases the oxidation state of the interfacial Ru, thus inducing a coordination chemical bonding of water species. The donor engages in transient bonding, during which the electron is transferred with higher reactivity as a result of increased molecular electronic order (improved molecular structure and decreased entropy). Water can thus be oxidized in successive steps involving stepwise changes of interfacial Ru complexes. For Ru chalcogenides, the efficiency of oxygen evolution from water depends on the density and purity of d states in the energy band with which electrons are exchanged (*10*). Electron transfer is thus enabled and supported by chemically induced ligand attachment and reorganization, which we may call passive self-organization.

Interfacial coordination electrochemistry, based on electron transfer through an energy band derived from transition metal d states (11), has yielded interesting new catalysts, among them materials containing Ru clusters that are very effective in reducing oxygen in fuel cells (12). They are also very selective in being simultaneously insensitive toward additional species such as methanol. This selectivity, for an illuminated FeS_2 electrode, also means that it will be highly efficient in photocurrent generation and remain entirely stable against photocorrosion in the presence of iodide as electron donor, which can attach as a ligand, but will have low efficiency and be unstable against corrosion in the presence of a comparable concentration of Fe^{2+} ions. The photocurrents involved can be selectively inhibited with suitable inorganic and organic species, and therefore the electron transfer reactions are site specific. This means that iodide is oxidized by coordination chemical attachment to the interfacial oxidized pyrite-iron, whereas the Fe^{2+} species are exchanging electrons at neighboring sites by tunneling processes or with interfacial sulfur acting as a bridge (Fig. 1) (13). Such a site specificity is not described by classical treatments of interfacial electron transfer, which consider the collective densities of state of an electrode and the statistical molecular behavior in its rate constants and not the local chemical environment and its ability to engage in transient chemical bonding.

These results emphasize the need for a more elaborate electron transfer theory that considers the local electron density distribution and the resulting strong chemical interactions. They also emphasize the importance of a medium, which participates in the electron transfer process by allowing passive chemical self-organization. This conclusion is supported by the ease with which photooxidation of water is accomplished by electrode materials, which provide such reaction possibilities during electron transfer.

Active Medium, Dynamic Self-Organization

A passive, thermally acting medium or a chemically participating medium for electron transfer, engaged in passive self-organization, is not the only prospect for electron transfer. Because an electron flux is a nonequilibrium process, it can be subject to conditions of nonlinear irreversible thermodynamics and pushed to conditions where dynamic self-organization is possible. Because heat transfer across a Benard system (heated viscous liquid in a temperature gradient) can be substantially accelerated during the autocatalytic formation of organized fluid patterns, electron transfer should be improved during molecular self-organization. In both cases, the critical conditions are autocatalytic loops, which draw a small fraction of the energy from the main energy flux.

A key requirement for molecular electronic self-organization is that, during electron transfer, a small amount of energy is not dissipated (passive molecular friction) but is provided by the external energy source (positive friction). Therefore, the medium is required to be active in the sense that it supplies some amount of temporarily stored energy (for example, in the form of phononic excitations or of conformational energy) to accelerate the electron transfer step.

The kinetics of molecular reactions can be dominated by irreversible thermodynamics and self-organization (14). We expect that the same is true for electron transfer mechanisms and that relevant biological energy conversion processes involving multielectron transfer at environmental temperature (nitrogen fixation and photosynthetic oxygen evolution from water) may take advantage of its remarkable possibilities (15).

In attempting to describe self-organization processes on a mesoscopic and microscopic scale, one principal difficulty arises: Self-organization requires the coupling of several subprocesses by means of positive and negative feedback loops, which leads on the mathematical level to genuine nonlinear equations. The classical theories for reaction rates, however, are based mainly on linear relations. Thus, for example, in the Marcus theory, the approximation of an ensemble of noninteracting oscillators modeling the polarizational fluctuations of the medium was used. In contrast, the individual oscillators in an active medium capable of generating positive feedback loops cannot be separated because of the nonlinear interactions between them. The Kramers theory is also a linear theory, but fortunately it is possible to generalize the basic Kramers equation to the case of nonlinear friction forces. The Kramers theory models a chemical reaction as a Brownian motion of a particle in a potential well created by a stochastic-acting environment (Fig. 2A). This environment is modeled by two terms, a

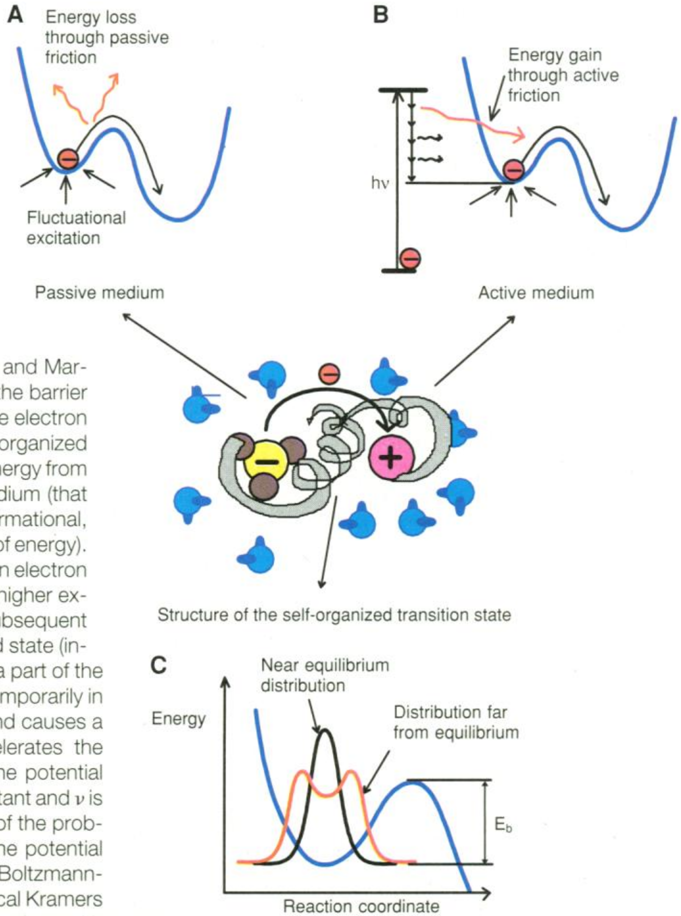

Fig. 2. Schematic comparison of the electron transfer interacting in different ways with the environment (here symbolized by water molecules and macromolecular protein helices). (**A**) Ordinary electron transfer driven by the medium fluctuations and hindered by passive frictional interaction with the medium, as described by the theories of Kramers and Marcus. In (A), the crossing of the barrier from left to right denotes the electron transfer process. (**B**) Self-organized electron transfer drawing energy from a temporarily activated medium (that is, a medium storing conformational, phononic, or related forms of energy). Here, a light quant excites an electron from the ground state to a higher excited state. During the subsequent relaxation to a lower excited state (inside the left potential well), a part of the released energy is stored temporarily in the surrounding medium and causes a negative friction that accelerates the electronic motion across the potential barrier; *h* is the Planck constant and ν is the frequency. (**C**) Shapes of the probability distributions inside the potential well: the near-equilibrium Boltzmann-like distribution in the classical Kramers problem (black line) in comparison with the nonequilibrium distribution according to the self-organized activated complex (red line) in the case of active friction. In the latter case, the substantially broadened distribution increases the probability of the system crossing the barrier with the activation energy E_b.

stochastic force exciting the particle and a systematic, velocity-dependent friction force drawing kinetic energy from the particle. The probability per unit time of the particle escaping from the well then gives the reaction rate constant for high and medium magnitudes (k_{high}) of the friction coefficient η:

$$k_{\mathrm{high}} = \frac{1}{\omega_C}\left[\sqrt{\frac{\eta^2}{4} + \omega_C^2} - \frac{\eta}{2}\right]k_0 \quad (4)$$

where ω_C is the oscillator frequency at the top of the potential barrier and k_0 is the classical TST result as an upper limit:

$$k_{\mathrm{TST}} = \frac{\omega_A}{2\pi}\exp\left(-\frac{E_b}{k_B T}\right) \quad (5)$$

where ω_A is the frequency at the bottom of the well and E_b is the energetic barrier height. For very small friction magnitudes, another expression for the rate constant (k_{low}) was derived showing a direct proportionality to the friction coefficient:

$$k_{\mathrm{low}} = \eta\frac{I_C}{k_B T}k_{\mathrm{TST}} \quad (6)$$

where I_C is a constant describing the action integral of the system, which corresponds to the motion across the barrier top.

The friction force in the classical Kramers theory is positive and constant. If one instead uses a friction force that depends on the main energy of the system, that is, negative for small energy values but positive for larger energy values, a positive feedback in the motion occurs. This positive feedback leads to self-sustained and stable oscillations with a well-defined amplitude (a so-called limit cycle in the theory of nonlinear systems). A well-known example is the Van-der-Pol oscillator, which describes autonomous oscillations in electric circuits with a positive feedback. Another example is the violine string, which gains energy through the friction with the bow and is excited to stable self-organized oscillations. It turns out that such Van-der-Pol–like nonlinear friction represents the simplest way to model an active medium, which is, under certain conditions, able to accelerate the molecular motion (Fig. 2B).

The thus modified Kramers equation describes the stationary probability distribution of the system state. Despite the long history of the Kramers theory, only recently have two research groups succeeded independently in solving this equation analytically for arbitrary magnitudes of the friction coefficient (*16*, *17*). Before these studies, only separate solutions for either very small or medium and strong friction forces were obtained, and several semiempirical interpolating formulas to overcome this "turnover problem" were suggested. The method developed by Naeh *et al.* (*17*), which uses the theory of matched asymptotic expansions in a very clever way, was shown to be generalizable for the case of nonlinear friction forces. Thereby, it was possible to obtain a solution of the turnover problem of the modified nonlinear Kramers equation describing the occurrence of self-organized oscillations during the rate process (*18*). The resulting expression for the rate of self-organized electron transfer shows a quadratic exponential dependence on the height of the activation barrier E_b as well as on two new parameters describing the energy content E_D of the surrounding active medium and the magnitude α of the feedback coupling to the medium. The maximum of this expression represents the analog to the TST limit of the classical Kramers approach:

$$k_{\mathrm{TST}} = \frac{\omega}{2\pi}\sqrt{\frac{\alpha k_B T}{2\pi f_C^2}}\exp\left(-\frac{\alpha(E_b - E_{LC})^2}{2k_B T}\right)$$
$$f_C = \alpha(E_b - E_{LC}),\ E_{LC} = E_D - 1/\alpha \quad (7)$$

where ω is the oscillation frequency at the bottom of the well, f_C is a parameter depending on the activation properties, and E_{LC} denotes the mean energy of the arising limit cycle oscillations inside the well. Under appropriate conditions, this rate constant can exceed the classical TST result by several orders of magnitude. This result seemingly contradicts the fact that the classical TST result represents the upper limit for thermally activated reaction rates. The solution of this paradoxical situation is that the classical TST result as a limiting case of the classical Kramers problem depends implicitly on the probability distribution of the medium fluctuations, which is Boltzmann-like (the maximum of the distribution is located at the origin of the phase space, $x = p = 0$, where x is the location and p is the momentum of the Brownian particle). In contrast, the TST-like limit of the self-organized nonlinear Kramers problem also depends on the underlying distribution function, which has non–Boltzman-like properties (the maximum is not located at the origin and forms a "crater" in the two-dimensional phase space; Fig. 2C). This remarkable broadening of the distribution function leads to a substantial increase in the probability of the system reaching the barrier top and therefore escaping the well. This increase in escape probability turns out to be a purely nonequilibrium effect that is only possible as long as the surrounding medium is energized.

The form of the exponent in the expression for the self-organized electron transfer requires further comment: The quadratic dependence in the exponent differs from the usual linear Arrhenius-like dependence in the TST but formally resembles the quadratic dependence in the Marcus formula. This latter coincidence seems to be rather accidental: The quadratic form of the Marcus exponent follows from the assumption of simple parabolic potential functions describing the reactants and the products, respectively. On the other hand, the quadratic form in the formula for the self-organized electron transfer results from the equally simple assumption of a linear dependence of the active friction coefficient on the mean system energy. The physical reasons for both rate constant expressions, however, are very different. The acceleration effect in the Marcus theory is a result of the increase of the thermodynamic driving force of the reaction. In contrast, the acceleration of the self-organized reaction rate results from the formation of a temporary nonequilibrium state of the medium (which should not be confused with the single "nonequilibrium fluctuations" in the Marcus theory, which follow a quasi-equilibrium distribution).

The phenomenologically derivable cooperative multielectron transfer (*19*), in which electrons are no longer transferred independently (as assumed in classical multielectron transfer theory) but are dependent on each other, may be understood in the following way: An initiating electron transfer event triggers subsequent ones by producing "positive friction" loops. If this nonlinear feedback is adequately adjusted, the electrons will be transferred in a cooperative way, not permitting intermediates, which may interfere in defining the electrochemical potential of the total reaction. Many enzymes in biology may function in such a cooperative way. An example is cytochrome C_3, which contains four heme groups. When one heme exchanges an electron, all others change their redox potential (*20*). The chance of developing such catalysts for real multielectron transfer would obviously be a great challenge for energy conversion catalysis. First, possible model systems may be seen in multicenter transition metal catalysts studied by Anson *et al.* (*21*), which permit mutual interaction through the chemical "backbone" structure.

Conclusion and Outlook

The improvements of electron transfer that we have discussed, as compared with classical electron transfer, have to do with a better management of entropy. Photoinduced coordination electrochemistry (Fig. 1B) may be understood as a passive self-organization. The local chemistry that is created at the beginning of electron transfer leads to a self-assembly of reactants, which substantially improves electron transfer efficiency and selectivity. Providing a positive molecular friction, equivalent to an autocatalytic loop (Fig. 2, B and C), may be understood as dynamic self-organization. Here, order is generated far from equilibrium by local export of entropy during an entropy-producing irreversible reaction. Substantially improved activation complexes may be formed for individual as well as cooperative multiple electron transfer.

A main challenge for the future will be understanding, designing, and controlling molecular chemical environments of electron-exchanging centers involving passive or dynamic self-organization. Passive self-organization is very attractive for energy conversion catalysis, because small molecules such as water or oxygen can efficiently be involved in electron transfer. Electron flow through the energy bands of catalytic electrode materials must be designed in such a way as to permit passive self-organization as shown for semiconductor materials with d energy band character.

The detailed structural properties of molecular systems necessary to make dynamic, self-organized electron transfer possible are still unknown. But it seems to be clear that the structure of the reacting molecules together with the macromolecular environment should be organized in such a way that it can temporarily store a part of the energy input. This energy can be stored as potential energy (conformational energy) or as kinetic energy (lattice oscillations) as well. A possible mechanism fitting into the proposed simple model would be the generation of phonons caused by the partial radiationless relaxation of the excited system. Given appropriate geometrical and mechanical properties of the surrounding protein structure, the movement of the phonons can become a directed flow (so-called phonon wind). This momentum flow acts like a negative friction on the reaction center, thus transferring some part of the relaxation energy to the reacting subsystem. The practical design of such dynamic molecular self-organization for electron transfer remains a substantial challenge for theoretical and synthetic chemistry.

A possible model system may be the 20-fs fast electron transfer from excited ruthenium complexes into nanocrystalline titanium dioxide (*8*). The electron density cloud of the electron during transfer may temporarily improve the polar bond between sensitizer and acceptor (positive friction), thus increasing the momentary electron transfer rate in an autocatalytic way. The result would be a drastically increased overall reactivity as shown for dynamic, self-organized electron transfer. Cooperative multielectron transfer may, on the other hand, already occur in biological systems that have developed self-organization to a high perfection. Although the catalytic function of the nitrogenase or the manganese complex (*22*) of photosynthetic oxygen evolution, after resolution of essential details of the molecular structures, is still not very clear on the basis of classical understanding of electron transfer, it may be possible to understand them as a self-organizing nonlinear system for multielectron transfer. Here, we have to be prepared to accept that highly nonlinear systems often escape simple chemical intuition.

REFERENCES AND NOTES

1. S. Gladstone, K. Laidler, H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
2. H. A. Kramers, *Physica* **7**, 284 (1940).
3. R. A. Marcus, *J. Chem. Phys*. **24**, 966 (1956); *ibid*., p. 979; *Can. J. Chem*. **37**, 155 (1959); *J. Phys. Chem*. **67**, 853 (1963); *J. Chem. Phys*. **43**, 679 (1965); R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985). For an overview of recent developments with contributions by Marcus, H. B. Gray, and others, see the proceedings of the conference "Electron Transfer in Proteins and Supramolecular Assemblies at Interfaces" (17 to 20 March 1996, Kanagawa, Japan) [*J. Electroanal. Chem*. **438**, 1–267 (1997)].
4. H. Taube, *J. Am. Chem. Soc*. **77**, 4481 (1955); N. S. Hush, *J. Chem. Phys*. **28**, 962 (1958); *Prog. Inorg. Chem*. **8**, 391 (1967); V. G. Levich and R. R. Dogonadze, *Dokl. Akad. Nauk SSSR Ser. Fiz. Khim*. **124**, 123 (1959); R. R. Dogonadze, A. M. Kuznetsov, M. A. Vorotyntsev, *Phys. Status Solidi B* **54**, 425, (1972); J. Ulstrup, *Charge Transfer Processes in Condensed Media* (Springer-Verlag, Berlin, 1979); J. Jortner, *Biochim. Biophys. Acta* **594**, 193 (1980).
5. M. Bixon, J. Jortner, M. E. Michel-Beyerle, in *The Photosynthetic Bacterial Reaction Center II*, J. Breton and A. Vermeglio, Eds. (Plenum, New York, 1992), pp. 292–308; M. Newton, *Chem. Rev*. **91**, 767 (1991).
6. H. Gerischer, *Z. Phys. Chem*. **26**, 223 (1960); *Adv. Electrochem. Electrochem. Eng*. **1**, 139 (1961).
7. H. Sumi and R. A. Marcus, *J. Chem. Phys*. **84**, 4894 (1985); L. D. Zusman, *Chem. Phys*. **49**, 295 (1980).
8. T. Hannappel, B. Burfeindt, F. Willig, *J. Phys. Chem. B* **101**, 6799 (1997).
9. H. Taube and H. Myers, *J. Am. Chem. Soc*. **76**, 4035 (1954); C. Creutz and H. Taube, *ibid*. **91**, 3988 (1969).
10. H.-M. Kuehne, W. Jaegermann, H. Tributsch, *Chem. Phys. Lett*. **112**, 160 (1984).
11. H. Tributsch, *J. Photochem*. **29**, 89 (1985); W. Jaegermann and H. Tributsch, *Prog. Surf. Sci*. **29**, 1 (1988); H. Tributsch, *Sol. Energy Mater. Sol. Cells* **31**, 548 (1994); N. Alonso-Vante and H. Tributsch, in *Electrochemistry of Novel Materials, Frontiers of Electrochemistry*, J. Lipkowski and P. N. Ross, Eds. (VCH, New York, 1994), pp. 1–63.
12. N. Alonso-Vante and H. Tributsch, *Nature* **323**, 431 (1986); N. Alonso-Vante, M. Gierig, H. Tributsch, *J. Electrochem. Soc*. **138**, 639 (1991).
13. W. Seeliger, G. L. Throughton, N. Alonso-Vante, H. Tributsch, *J. Electrochem. Soc*. **142**, 166 (1995).
14. P. Glansdorf and I. Prigogine, *Thermodynamics of Structure, Stability and Fluctuations* (Wiley, New York, 1971).
15. H. Tributsch and L. Pohlmann, *J. Electroanal. Chem*. **396**, 53 (1995).
16. E. Pollak, H. Grabert, P. Hänggi, *J. Chem. Phys*. **91**, 4073 (1989).
17. T. Naeh, M. M. Klosek, B. J. Matkowsky, Z. Schuss, *SIAM J. Appl. Math*. **50**, 595 (1990).
18. L. Pohlmann and H. Tributsch, *Electrochim. Acta* **42**, 211 (1997).
19. ———, *J. Theor. Biol*. **155**, 443 (1992); *ibid*. **156**, 63 (1992).
20. K. Niki, T. Yagi, H. Inokuchi, K. Kimura, *J. Electrochem. Soc*. **124**, 1889 (1977).
21. B. Steiger and F. C. Anson, *Inorg. Chem*. **33**, 5767 (1994).
22. D. M. Proserpio, R. Hoffmann, G. C. Dismukes, *J. Am. Chem. Soc*. **114**, 4374 (1992).
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