Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the Franklin Institute 342 (2005) 586–591

Journal of The Franklin Institute

www.elsevier.com/locate/jfranklin

The 2004 Benjamin Franklin Medal in Chemistry presented to Harry B. Gray

Klaus H. Theopold*

Department Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

Abstract

The Franklin Institute, Philadelphia, Pennsylvania, awarded the 2004 Benjamin Franklin Medal in Chemistry to Harry B. Gray for his pioneering contributions in the field of electron transfer in metalloproteins. In a series of elegant and challenging experiments beginning in the late 70s, Gray and his coworkers have shown that the transfer of electrons in metalloproteins can proceed over long distances (˜ 20 Å) and at fast rates. These experiments have involved the regiospecific functionalization of structurally characterized electron transfer proteins with ruthenium complexes, coupled with laser excitation and transient spectroscopy. Probing the effects of thermodynamic driving force, temperature, donor–acceptor distance and electronic coupling, Gray has shaped our detailed current understanding of the principles governing biological electron flow. The mechanism of electron transfer has been identified as electron tunneling mediated by the molecules separating donor and acceptor. Tunneling timetables have been established for various intervening media. Important biological processes like respiration and photosynthesis depend on facile electron transfer, and Gray's contribution serves as the fundamental basis for understanding these and many related reactions.

Keywords: Electron transfer; Proteins; Franklin medal

---

*Tel.: +1 302 831 1546; fax: +1 302 831 6335.
E-mail address: theopold@udel.edu.

0016-0032/$30.00 © 2005 The Franklin Institute. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfranklin.2005.04.015

1. Introduction and background

Redox reactions, i.e. reactions involving reduction (addition of electrons) and oxidation (removal of electrons), are among the most important and fundamental chemical transformations. Beyond the obvious thermodynamic constraints, which are readily understood in terms of the redox potentials of electron donors and acceptors, there also arise kinetic considerations. Rates of electron transfer reactions span a wide range, and the investigation of the mechanisms and rates of electron transfer — in particular between metal complexes—has been an active area of research in the second half of the twentieth century [1].

Two major classes of reactions have been identified, namely 'inner sphere' and 'outer sphere' electron transfer processes. The former involve facilitation of the electron transfer through bridging ligands; they are exemplified by the classic reaction of two coordination compounds in aqueous solution shown in Eq. (1) [2]:

$$\left[\mathrm{C}_{\mathrm{o}}^{\mathrm{III}}(\mathrm{NH_3})_5\mathrm{Cl}\right]^{2+} + \left[\mathrm{Cr^{II}(OH_2)_6}\right]^{2+} \rightarrow \left[\mathrm{Co^{II}(OH_3)_6}\right]^{2+} + \left[\mathrm{Cr^{III}(OH_2)_5Cl}\right]^{2+} + 5\,\mathrm{NH_3}. \tag{1}$$

Outer sphere electron transfer, on the other hand, merely relies on momentary close approach of the reactants by diffusion. Much effort has been expended on the determination of rates of 'degenerate self exchange reactions' [3], such as the one given in Eq. (2), an acknowledged outer sphere electron transfer.

$$\left[\mathrm{Fe^{II}(OH_2)_6}\right]^{2+} + \left[\mathbf{Fe}^{\mathrm{III}}\mathrm{(OH_2)_6}\right]^{3+} \rightarrow \left[\mathrm{Fe^{III}(OH_2)_6}\right]^{3+} + \left[\mathbf{Fe}^{\mathrm{II}}\mathrm{(OH_2)_6}\right]^{2+},$$
$$k_{\mathrm{et}}(22^\circ\mathrm{C}) = 3.3\mathrm{M^{-1}s^{-1}}, \Delta G^{\ddagger} = 16.7\,\mathrm{kcal/mol}. \tag{2}$$

Such thermoneutral reactions ($\Delta G^0 = 0$) provide intrinsic activation barriers unaffected by a thermodynamic driving force. In 1983 Henry Taube won the Nobel Prize in Chemistry for his experimental work in the area of electron transfer reactions [4].

In parallel to the experiments, a theoretical treatment of outer sphere electron transfer was developed by Marcus [5]. His theory, summarized in expressions such as Eq. 3, allowed the calculation of activation barriers and absolute rate constants from first principles, taking into account reorganization energies (λ), thermodynamic driving forces (ΔG^o), and electronic coupling between donor and acceptor (H_{AB}) [6]:

$$k_{\mathrm{et}} = \left(4\pi^3/h2\lambda k_{\mathrm{B}}T\right)^{1/2} H_{\mathrm{AB}}^2 \exp\left[-(\Delta G^o + \lambda)^2/4\lambda k_{\mathrm{B}}T\right]. \tag{3}$$

Rudi Marcus won the 1992 Nobel Prize in Chemistry for the development of the theory that carries his name [7].

Electron transfer processes play a vital role in biology [8]. Life sustaining processes such as respiration, photosynthesis, nitrogen fixation, and many others rely on the transfer of electrons between biomolecules. However, biological electron donors and acceptors — typically metal complexes — are often shrouded in proteins, preventing them from attaining close contact. Based on the established notions about electron transfer reactions, such long transfer distances should lead to extremely slow electron transfer rates. And yet, electrons are apparently transferred, over distances