1987 PROGRAM

A.M.

9:00 **Registration and Coffee—Chemistry-Physics, Rm. 137**

9:30 **Welcome by Dean Wimberly C. Royster, Vice-Chancellor for Research, University of Kentucky, Chemistry-Physics, Rm. 139**

9:35 **Introductory Remarks**

9:40 **Dr. George McLendon, University of Rochester**
Birds Do It, Bees Do It: How Does Biology Transport Electrons?

Biological energy is channeled via a series of simple electron transfer reactions. A brief overview will be presented of how electron transfer occurs over long distances in simple chemical systems. This work demonstrates that electron transfer reactions can occur rapidly ($<10^6 s^{-1}$) even when the reactants do not collide and are widely separated (eg 15 Å). The recent results fully support the predictions made by Marcus and Hopfield some time ago.

10:40 **Break**

10:50 **Dr. William H. Orme-Johnson, Massachusetts Institute of Technology**
Electron Transfer and Biological Nitrogen Fixation

In organisms that can utilize metabolic energy derived from carbohydrate metabolism to carry out the reduction of atmospheric nitrogen to ammonia, a specialized set of enzymes oxidizes pyruvate and conveys to dinitrogen the reducing equivalents thus obtained. Through the four proteins participating directly in this process, the eight electrons ultimately used during the reduction of one N_2 molecule are passed one at a time. For the case of the free-living nitrogen fixer *Klebsiella pneumoniae*, an essentially complete genetic analysis suggests that seventeen genes are required to synthesize and regulate the components of the nitrogen fixation system. Using the tools of genetic engineering as well as spectroscopic procedures, the nature of the prosthetic groups required for electron transfer and the chemistry they catalyze is being explored. Novel features of this complex system, perhaps of more general significance, include the use of metal centers to do the $2e^-/1e^-$ transformer separation normally carried out by flavins, the utilization of a low molecular weight protein electron carrier (flavodoxin) operating at nearly diffusion - controlled rates, the coupling of MgATP hydrolysis to low potential electron transfer, and the accumulation of multiple elections in $1e^-$ storage sites in the N_2-reducing component.

11:50 **Discussion**

P.M.

12:15 **Buffet Lunch, Faculty Club**
(Please return card by April 15, 1987 for reservation. Cost $6.00 to be paid at registration.)

1:30 **Dr. Harry B. Gray, California Institute of Technology**
Long-Range Electron Transfer in Heme Proteins

Kinetic experiments at Northwestern, Rochester, Brookhaven, and Caltech have conclusively shown that electrons can be transferred relatively rapidly over large distances (greater than 10 angstroms) in proteins. Current research focuses on the factors that determine the rates of these long-range electron transfers in modified proteins and protein complexes. Experiments on ruthenium-modified myoglobins and cytochromes have examined the roles of distance and donor-acceptor structures and energetics on the reactions: this work has shown that protein electron-transfer rates decrease exponentially with the donor-acceptor edge-to-edge distance. Evidence that an intervening aromatic residue enhances long-range donor-acceptor electronic coupling has been obtained in studies of electron transfer from the excited triplet state of a zinc porphyrin to a ruthenium acceptor in a doubly substituted myoglobin. Recent work involving systematic variations in donor-acceptor energetics has defined experimentally the reorganization energies for protein electron transfer

2:30 **Break**

2:40 **Dr. Brian M. Hoffman, Northwestern University**
Long-Range Electron Transfer Between Proteins

We are using the technique of metal replacement within hemoproteins to study of long-range (ca. 25 Å) electron tunnelling in protein complexes that incorporate redox centers rigidly held fixed at crystallographically known distance and orientation. One system we employ is the mixed-metal hybrid hemoglobins having one type of chain substituted with a closed shell metalloporphyrin, for example the [Zn,Fe^{III}] hybrids. In addition, we study the complex between cytochrome c and metal-substituted cytochrome c peroxidase, in which case we directly monitor long-range intermolecular electron transfer between proteins that are natural redox partners. We find that variations in the protein matrix through use of naturally occurring variants or by site-directed mutagenesis can *dramatically* alter electron transfer rates.

3:40 **Discussion**

4:00 **Social Hour, Chemistry-Physics, Rm. 137**

We encourage symposium participants, especially students, to take this opportunity to meet with the speakers.

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Anna S. Naff

ELECTRON TRANSFER IN METALLOPROTEINS

Speakers

HARRY B. GRAY
BRIAN M. HOFFMAN
GEORGE McLENDON
WILLIAM H. ORME-JOHNSON

Monday, April 24, 1987
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