ORGANIC & INORGANIC PHOTOCHEMISTRY

Organic and Inorganic Photochemistry

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Organic and Inorganic Photochemistry

MOLECULAR AND SUPRAMOLECULAR PHOTOCHEMISTRY

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2. Organic and Inorganic Photochemistry, *edited by V. Ramamurthy and Kirk S. Schanze*

ADDITIONAL VOLUMES IN PREPARATION

Preface

The science of chemistry has entered an era when techniques of chemical structure analysis are sufficiently sophisticated to render routine the elucidation of amazingly intricate molecular structures. These relatively recent technological advances now allow chemists to carry out detailed investigations of highly complex synthetic and naturally occurring (biological) molecular systems from the molecular perspective. Thus has been born the field of "supramolecular chemistry"—the molecular-level study of complex arrays or assemblies consisting of many basic molecular building blocks held together by weak intermolecular forces. Photochemists have led the charge into this new frontier of chemical science, and therefore it is appropriate that this second volume of the Molecular and Supermolecular Photochemistry series highlights state-of-the-art research of complex naturally occurring and synthetic supramolecular arrays.

During the past decade it has become increasingly clear that the structure and function of polydeoxyribonucleic acid (DNA) can be modified significantly by binding to small molecules. Complexes formed by noncovalent interactions between DNA and small organic and inorganic molecules are examples of supramolecular arrays that provide the basis for drug action and for analytical (sensing) of specific sequences of DNA base pairs. The first two chapters in this volume feature recent work concerning the mechanism by which transition metal complexes bind to DNA and how this binding modifies the photochemical and photophysical properties of the bound complexes and the DNA "scaffold." In particular, both chapters explore the interesting topic of photoinduced electron transfer between intercalated molecules and address the ongoing question as to whether DNA can act as a "molecular wire."

Molecular electron transfer is the basis for many important natural and commercial processes. During the past decade photochemists have relied upon supramolecular arrays of molecules to facilitate their understanding of the chemical and physical basis for this fundamentally important process. It therefore seems appropriate that several chapters in this volume examine thermally and photochemically induced electron transfer in supramolecular assemblies consisting of inorganic molecular building blocks such as covalently linked donor–acceptor "dyads," transition metal clusters, and nanocrystalline semiconductor particles.

Liquid crystalline polymers and molecular organic crystals are examples of supramolecular arrays in which long-range order plays an important role in determining the photophysical and photochemical properties of the system. Two chapters in the present volume explore the properties of liquid crystalline polymers and molecular crystals, with an emphasis on understanding how the structure of the supramolecular organization guides the course of the photochemical reactivity and photophysical properties of the component molecular units.

Progress in supramolecular photochemistry is intimately linked with the progress and understanding of the photochemical behavior of molecular systems. With recent advances in time-resolved techniques it has become possible to study the excited state behavior of reactive intermediates as well as that of higher excited states. A chapter on this topic is also included in this volume.

Although the science of molecular photochemistry remains very active, there is no doubt that in the future photochemists will focus increasingly on supramolecular chemical structures and arrays. This trend is a natural progression as the science of photochemistry meets the demands of new technologies based on advanced materials and as the ability increases to probe complex (photo)biological processes at the molecular level.

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1

A Comparison of Experimental and Theoretical Studies of Electron Transfer Within DNA Duplexes

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I. INTRODUCTION

This chapter introduces an active and provocative area of current research. It describes motivations for studying electron transfer (ET) chemistry in general and ET reactions in (2′-deoxyribonucleic acid) DNA in particular. Rate expressions for quantum mechanical and semiclassical electron transfer models are given along with a description of appropriate conditions for their use. Formulas describing the distance dependence of electronic coupling (H_{AB}) and solvent reorganization energy are also discussed as a basis for understanding and interpreting recent experiments. Five different long-range ET experiments are presented in detail, and their results are compared with one another and with the results of similar experiments in proteins. Discrepancies and difficulties are noted, and suggestions for new experiments are made. Importantly, the experimental results are analyzed and discussed in light of recent semiempirical CNDO/S level quantum mechanical calculations of H_{AB} in DNA involving super-size sets of valence electrons. The chapter also contains descriptions of how photoinduced ET reactions in RNA are used to understand the operation of ribozymes (catalytic RNA) and of recent studies that demonstate (1) long-range migration of oxidative damage to DNA single strands in DNA–DNA and peptide nucleic acid (PNA)–DNA duplexes, (2) long-range oxidative thymine dimer (T^T) scission in DNA duplexes, and (3) migration of excess photoinjected electrons in DNA duplexes. The chapter concludes with a description of the best measurement todate of the decay of electronic coupling in DNA duplexes with increasing distance of donor/acceptor (D/A) separation, $\beta = 0.64 \pm 0.1$ Å^{-1}. This value of β, however, is for ET transfer from a guanosine nucleotide to the excited state of a doubly tethered stilbene acceptor. Whether β would be as low if DNA bases themselves were not directly involved as electron donors or acceptors is not yet known.

II. WHY ARE ELECTRON TRANSFER (ET) REACTIONS INTERESTING?

From a chemical perspective, ET reactions are the simplest kind of process in which reactants are changed into products. The process, although complex on a microscopic scale, has the important simplifying feature that the nuclei do not move while the chemically significant electron changes its location and turns reactants into products [1,2]. This fact makes detailed theoretical calculations of ET reactions possible, and thus provides chemists with a precise way of summarizing experimental results and of designing new experiments both to refine the understanding of the molecular basis of ET chemistry and to use this chemistry in purposeful ways. From a practical perspective, ET chemistry is responsible for life as we know it on Earth [3,4]. This is true because photosynthesis in plants and bacteria is at its core based on nature's ability to assemble a number of electrochemically active molecules in the right relative locations so that when they absorb light an ET reaction occurs [5]. In fact much research on photoinduced ET reactions in the past three decades has demonstrated that getting the first charge transfer to occur is not hard [6–8]. The key to photosynthesis is that the oxidized donor ($D^{\cdot +}$) and the nearby reduced acceptor ($A^{\cdot -}$) do not immediately back-react to re-form the starting molecules [9]. In fact, in bacterial photosynthesis nearly all of the electrons transferred to the primary acceptor are successfully transferred to secondary acceptors [5,10–14]. The important consequence of this secondary ET chemistry is that plants, upon which we and most other animals depend, grow. However, our dependence on ET chemistry does not end with photosynthesis. When we eat food, we acquire both energy and the molecular building materials needed to sustain our lives. ET reactions in our mitochondria reverse the photosynthetic process by consuming plant-produced carbohydrates and thereby provide us with the energy we need to live [15]. Our respiratory ET chemistry is in fact a highly controlled oxidation (or "burning") of plant fuel.

A. What Is Interesting About ET in DNA?

From a chemical perspective, the double-helix produced by two intertwining strands of oligomeric DNA is a fascinating and unique molecular structure. (See Fig. 1 for a structural model of a 12-base pair duplex of B-form DNA.) In it nucleic acid bases are stacked in pairs one on top of the other with a slight twist reminiscent of a spiral staircase [16]. The unique stacking and overlapping of the *n*- and π-electrons of DNA bases may provide a preferred path for electron transfer. Similarly, the exceptional closeness of the stacked bases may have important consequences for charge motion in DNA duplexes. Additionally, the

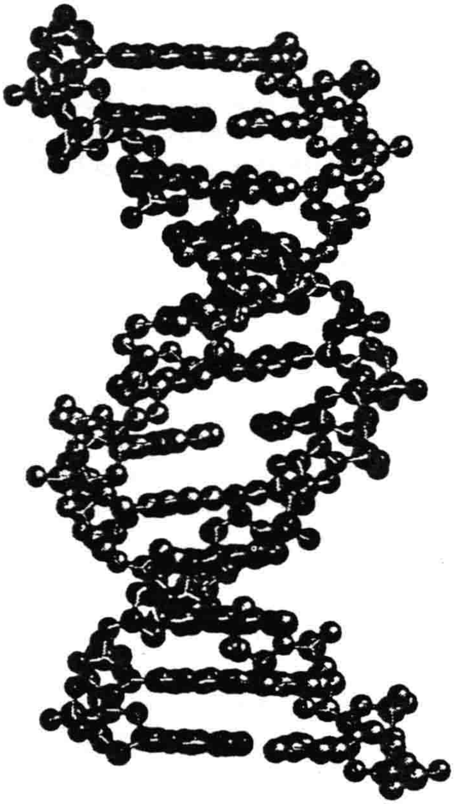

FIGURE 1 Molecular model of a 12-base pair duplex of canonical B-form DNA. The two 12-mer strands that intertwine to form the duplex are colored separately (black and gray). Nucleic acid base pairs are stacked perpendicular to the helical axis at 3.4-Å intervals (center-to-center distance), and the duplex helix repeats its spiral structure every 10 base pairs. (Figure provided by Dr. Carolyn Kanagy using the Sybyl Version 6.3 molecular modeling program from Tripos, Inc. and standard B-form DNA substructures.)

semirigid structure of a short DNA duplex makes it an attractive scaffold for creating an artificial photosynthetic reaction center. Research on both model and natural photosynthetic systems has demonstrated that the precise positioning of redox-active molecules is crucial for minimizing energy-wasting back-reactions and maximizing desired secondary ET reactions [17–24]. Thus, covalently substituting a DNA duplex with redox-active molecules offers a strategy for accurately controlling the position of desired redox-active chromophores.

From a health perspective, both radiation and natural cellular processes damage DNA and create reduced and oxidized ET products [25–34]. Fortunately, much of this damage is repaired shortly after it occurs by DNA repair enzymes. However, in some instances this is not the case, and tumors or cancer result. We would benefit from molecular information on the types of damage radiation produces and on the mechanisms that enzymes use to repair this damage. Radiation damage to DNA involves primary ionization steps as well as migration of charges to trap sites where irreversible chemical reactions occur [27,28,32,33]. Thus charge migration is a key step in both natural photosynthesis and artificial solar energy utilization, as well as in DNA radiation damage. Additional health benefits that are not directly related to ET chemistry also arise from ET research in DNA because the new synthetic methods developed to modify DNA for this research can also be applied to creating covalently modified DNA structures for use as drugs, medical diagnostic agents, or as tools for studying biomolecular processes (see below). For example, DNA-probe based diagnostic tests for bacterial and viral infections and for genetic defects may be improved, since these tests rely on the same DNA modification chemistry as does DNA ET research. Finally, research results on the mechanisms of DNA-mediated ET processes hold promise that entirely new ways of performing DNA diagnostic tests can be developed based on the ET properties of synthetically modified DNA strands.

III. THEORETICAL MODELS OF ET

To understand the factors that are important in controlling the rates of ET reactions, it is best to refer to a specific theoretical model [35]. Choosing a model defines terms and allows us to analyze the results of experiments in precise ways. There are two main types of models: classical and quantum mechanical. One way of smoothly moving from the use of a classical to a quantum mechanical model is provided by semiclassical (Landau–Zener) ET theory [36–38]. At high temperature, quantum mechanical models become equivalent in most respects to semiclassical ones. Thus the appropriate choice of model depends on the type of ET reaction that we are interested in studying. Ones in which the electron donor and acceptor have strong electronic interaction with each other prior to the ET event are well described by a classical model. In these systems an ET reaction always proceeds to products if the reactants reach the top of the reaction barrier (strong-interaction or adiabatic limit). In most biological ET processes (including photosynthetic ones), there is some chance (perhaps a very large one) that even if the reactants reach the top of the reaction barrier they will not proceed to products, but rather will relax back to starting materials without ET. Not surprisingly this occurs because the electron donor and acceptor have a weak electronic interaction with each other prior to the ET event. These types of ET reactions (weak-interaction or nonadiabatic) must be modeled quantum mechanically or semiclassically. An active area of current ET research involves calculating and measuring the magnitudes of electronic couplings in D/A systems.

A. Quantum Mechanical Models

Brunschwig and Sutin [39] building on the work of De Vault [2] and Jortner [40] give Eq. (1) as a quantum mechanical expression for the rate of electron transfer (k_{ET}) for when two vibrational modes are responsible for bringing the reactant and product configurations into an energy-matching configuration (usually the top of the reaction coordinate). Note that since the electron must transfer from the reactant configuration (D ... A) to that of the product ($\mathrm{D}^{\cdot+}$ ... $\mathrm{A}^{\cdot-}$) without nuclear rearrangement, the transfer must occur between isoenergetic states for energy is to be conserved.

$$k_{\mathrm{ET}} = \frac{2\pi^{3/2}H_{\mathrm{AB}}^{2}}{h}\left(\frac{1}{\lambda_s kT}\right)^{1/2} \exp\left[-S_f \coth\left(\frac{h\omega_f}{4\pi kT}\right)\right] \times \sum_{m=-\infty}^{m=+\infty} \exp\left(\frac{mh\omega_f}{4\pi kT}\right) I_{|m|}\left[S_f \operatorname{csch}\left(\frac{h\omega_f}{4\pi kT}\right)\right] \times \exp\left[-\frac{(\Delta E + mh\beta_f/2\pi + \lambda_s)^2}{4\lambda_s kT}\right] \quad (1)$$

$I_{|m|}[Z]$ is the modified Bessel function, defined as:

$$I_{|m|}[Z] = \sum_{k=0}^{k=\infty} \frac{(Z/2)^{m+2k}}{k!(m+k)!} \quad (2)$$

The following variables are used in Eqs. (1) and (2): H_{AB} is the electronic coupling matrix element that permits ET to occur; h is Planck's constant; k is Boltzmann's constant; T is absolute temperature; λ_s is the reorganization energy of the solvent vibrations associated with ET; ω_f is the angular frequency of the quantized, high-energy molecular vibration associated with ET, such that $\omega_f/2\pi = \nu_f$; m in the summation refers to the number of quanta in the high-frequency mode; S_f is the ratio of the high-frequency mode's reorganization energy (λ_f) to the energy of one quanta of energy of this mode ($h\nu_f$), $S_f = \lambda_f/h\nu_f$; and ΔE is the energy change in an ET reaction on going from reactants to products.

In fact, many vibrations may be involved in the ET reaction, but the above coarse grain theory focuses on two modes of vibrational motion. One mode has low energy ($h\nu_s$ or $h\omega_s/2\pi$) and is typical of solvent motions. Since quantum modes in this class have energy spacings that are much smaller than the energy of a room temperature bath ($h\nu_s \ll kT$), they act classically with continuously varying energy configurations. Their contribution to k_{ET} is governed by the λ_s reorganization energy parameter. The other vibrational mode has high energy, $h\nu_f$. In some studies its value has been taken to be 1500 cm^{-1} [41,42]. Note that specifying ν_s and either λ_f or S_f is sufficient, but it is usually more convenient to assign λ_f because it is conceptually similar to λ_s.

The energy change in an ET reaction is ΔE, and it is negative for exergonic (spontaneous) reactions. Inspection of the Gaussian term in Eq. (1) shows that it is strongly peaked for values of $m = 2\pi\,(|\Delta E| - \lambda_s)/h\omega_f$, which limits the range over which the sum must be calculated. In practice for photoinduced ET reactions, ΔE is obtained from electrochemical and excited state energy data according to [43]

$$\Delta E \approx \Delta G^\circ(\text{ET}) = e[E^\circ(\text{D}^{\cdot+}/\text{D}) - E^\circ(\text{A}/\text{A}^{\cdot-})] - E_{0,0}(\text{excited state}) + w(r) \tag{3}$$

where e is the charge on an electron; E° is a reduction potential; $\text{E}_{0,0}$ is the light-absorbing (D or A) chromophore's reactive excited state energy relative to its ground state; and $w(r)$ is a coulombic interaction term between oxidized donor and reduced acceptor which represents the free energy due to separating the ionic products a distance r relative to each other $w(\infty) = 0$ [44,45]. Generally, in polar media the coulombic term is less than ca. 0.1 eV and is neglected [36,46,47].

H_{AB} is the electronic coupling matrix element that links the initial and final electronic states. Note that k_{ET} depends on the square of this electronic coupling element. To a first approximation the magnitude of H_{AB} depends on the overlap of the donor and acceptor wavefunctions. For long-range electron transfer between donors and acceptors bound to proteins or DNA, H_{AB} can be viewed as depending on the interaction of donor and acceptor orbitals with the intervening bridge orbitals summed over all occupied and unoccupied molecular orbitals of the bridge. Importantly, the interaction with the bridge orbitals is multiplied by the inverse of an energy difference term, $1/(E_N - E_{\text{tun}})$, where E_N is the energy of the Nth bridge orbital and E_{tun} is the electronic energy of the activated complex (top of the reaction coordinate). This term has the effect of preferentially weighting low-lying electronic states of the bridge for the case in which E_{tun} is only slightly below or above these bridge states. For cases in which the energy difference between E_{tun} and the nearest bridge orbitals is large, k_{ET} is not expected to depend significantly on the tunneling energy [48,49].

Although the Eq. (1) rate expression appears formidable at first sighting, programs such as *Mathematica* [50] make evaluating it as a function of various