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Electron Transfer: A Critical Link between Subdisciplines in Chemistry

Electron transfer, one of the simplest of chemical events, profoundly affects chemical reactivity by inverting normal electron densities in an electron donor–acceptor pair, thus activating previously inaccessible reaction modes. To the extent that most energy, and all life, on earth derive ultimately from photosynthesis, our very existence depends on this fundamental process. It is hardly surprising, then, that examples of electron-transfer activation abound within every subdiscipline of science. It is virtually impossible to peruse either general or specialized scientific journals without encountering at least one or two articles dealing with the topic. This very diversity attests to the importance of an informative overview of the subject but simultaneously underscores the difficulty of providing a satisfactorily comprehensive summary.

Collected here are an assortment of brief reviews on a variety of topics relevant to chemical applications of electron transfer. The intent is to provide a critical retrospective of some specific scientific underpinnings for the experimental and theoretical basis by which electron transfer can be effectively controlled. These articles are selected, in part, to complement existing treatments and, especially, to introduce students to the concepts of electron transfer in a coherent manner. By considering such topics through the eyes of recognized leaders in this field, we hope to initiate even nonspecialists to the intriguing questions remaining in this area.

Included in this issue are seven reviews which describe electron transfer in well-defined inorganic and organic systems, with particular emphasis on the lessons to be learned from kinetics in describing the electron-transfer event. Thus, the contribution from Gray and Winkler describes electron transfer in native proteins modified by complexation with redox-active metal ions, while that of Isied, Ogawa, and Wishart focuses on the use of short peptides as a vehicle for studying electron transfer between two metal centers. McLendon and Hake describe how electron transfer between complex proteins addresses the next level of biological complexity. Jordan and Paddon-Row characterize the factors influencing electron transfer across rigid organic bridges, and Wasielewski summarizes recent progress in adopting largely organic supramolecular systems as models for artificial photosynthesis. Weaver provides an analysis of dynamic solvation on electron-transfer energy barriers, and Koval and Howard analyze the complexities introduced by studying electron transfers at the semiconductor–electrolyte interface.

Besides the contributions in this issue, this area has been reviewed with increasing frequency, reflecting its importance. Therefore, as a pedagogical aid, we also offer the following list of other reviews covering this area which have recently appeared in previous *Chemical Reviews* issues or topical monograph series.

Some recent relevant reviews published in *Chemical Reviews* in which electron transfer is a principal thrust are as follows:

Julliard, M.; Chanon, M. Photoelectron Transfer Catalysis: Its Connections with Thermal and Electrochemical Analogues. *Chem. Rev.* **1983**, *83*, 425.

Kavarnos, G. J.; Turro, N. J. Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples. *Chem. Rev.* **1986**, *86*, 401.

Mikkelsen, K. V.; Ratner, M. A. Electron Tunneling in Solid-State Electron-Transfer Reactions. *Chem. Rev.* **1987**, *87*, 113.

Andrieux, C. P.; Hapiot, P.; Saveant, J. M. Fast Kinetics by Means of Direct and Indirect Electrochemical Techniques. *Chem. Rev.* **1990**, *90*, 113.

Evans, D. H. Solution Electron-Transfer Reactions in Organic and Organometallic Electrochemistry. *Chem. Rev.* **1990**, *90*, 739.

Blondin, G.; Girerd, J.-J. Interplay of Electron Exchange and Electron Transfer in Metal Polynuclear Complexes in Proteins or Chemical Models. *Chem. Rev.* **1990**, *90*, 1359.

Newton, M. D. Quantum Chemical Probes of Electron Transfer Kinetics: The Nature of Donor–Acceptor Interactions. *Chem. Rev.* **1991**, *91*, 767.

Some other relevant reviews in recent monograph series are as follows:

Heterogeneous Photoinduced Electron Transfer; Grätzel, M., Ed.; CRC Publishers: Boca Raton, FL, 1988.

Photoinduced Electron Transfer; Fox, M. A.; Chanon, M., Eds.; Elsevier: Amsterdam, 1988:

Part A. *Conceptual Basis for Electron Transfer*

Schermann, J. P.; Astruc, J. P.; Desfrançois, C.; Barbé, R. Electron Transfer between Excited Atoms and Molecules.

Purcell, K. F.; Blaive, B. Theory of Electron Transfer Reactions.

Wasielewski, M. R. Distance Dependencies of Electron Transfer Reactions.

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of Long-Range Electron-Transfer Reactions in Solution.
Schmehl, R. H.; Ryu, C. K.; Elliott, C. M.; Headford, C. L. E.; Ferrere, S. Intramolecular Electron Transfer from Photoexcited Ru(II) Diimine Complexes to *N,N'*-Diquaternarized Bipyridines.
Ondrechen, M. J.; Gozashti, S.; Zhang, L.-T.; Zhou, F. Bridged Mixed-Valence Systems: How Polarizable Bridging Ligands Can Lead to Interesting Spectroscopic and Conductive Properties.
Marusak, R. A.; Shields, T. P.; Lappin, A. G. Chiral Recognition by Metal-Ion Complexes in Electron-Transfer Reactions.
Orman, L. K.; Anderson, D. R.; Yabe, T.; Hopkins, J. B. The Role of Free Energy in Interligand Electron Transfer.
Whangbo, M.-H. Band Orbital Mixing and Electronic Instability of Low-Dimensional Metals.
Goodenough, J. B. Ceramic Superconductors: Single-Valent versus Mixed-Valent Oxides.
Burdett, J. K.; Kulkarni, G. V. Geometrical Control of Superconductivity in Copper Oxide Based Superconductors.
Tonge, L. M.; Richeson, D. S.; Marks, T. J.; Zhao, J.; Zhang, J.; Wessels, B. W.; Marcy, H. O.; Kannewurf, C. R. Organometallic Chemical Vapor Deposition: Strategies and Progress in the Preparation of Thin Films of Superconductors Having High Critical Temperatures.
Rogel, F.; Zhang, J.; Payne, M. W.; Corbett, J. D. Centered Cluster Halides for Group-Three and Group-Four Transition Metals: A Versatile Solid-State and Solution Chemistry.
Bartlett, N.; Okino, F.; Mallouk, T. E.; Hagiwara, R.; Lerner, M.; Rosenthal, G. L.; Kourtakis, K. Oxidative Intercalation of Graphite by Fluoroanionic Species: Evidence for Thermodynamic Barrier.
Barrows, J. N.; Pope, M. T. Intramolecular Electron Transfer and Electron Delocalization in Molybdophosphate Heteropoly Anions.
Miller, J. S.; Epstein, A. J. Organometallic Electron-Transfer Salts with Tetracyanoethylene Exhibiting Ferromagnetic Coupling.
Bein, T.; Enzel, P.; Beuneu, F.; Zuppiroli, L. Stabilization of Conductive Heteroaromatic Polymers in Large-Pore Zeolite Channels.

Electron Transfer in Inorganic, Organic, and Biological Systems; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series 228, American Chemical Society: Washington, DC, 1991.
Bolton, J. R.; Mataga, N.; McLendon, G. Introduction to Electron Transfer in Inorganic, Organic, and Biological Systems.
Bolton, J. R.; Archer, M. D. Basic Electron Transfer Theory.
Sutin, N. Nuclear and Electronic Factors in Electron Transfer Reactions – Distance Dependence of Electron Transfer Rates.
Kakitani, T.; Yoshimori, A.; Mataga, N. Theoretical Analysis of Energy-Gap Laws of Electron Transfer Reactions-Distribution Effect of Donor-Acceptor Distance.
Beratan, D. N.; Onuchic, J. N. Electron Transfer—From Model Compounds to Proteins.
Mataga, N. Photoinduced Charge Separation and Charge Recombination of Transient Ion Pair States—Ultrafast Laser Photolysis.
Bolton, J. R.; Schmidt, J. A.; Ho, T. F.; Liu, J. Y.; Roach, K. J.; Weedon, A. C.; Archer, M. D.; Wilford, J. H.; Gadzekpo, V. P. Y. Solvent, Temperature, and Bridge Dependence of Photoinduced Intramolecular Electron Transfer.
Wasielewski, M. R.; Johnson, D. G.; Niemczyk, M. P.; Gaines, G. L.; O'Neil, M. P.; Svec, W. A. Solvent-Dependent Photophysics of Fixed-Distance Chlorophyll-Porphyrin Molecules—The Possible Role of Low-Lying Charge Transfer States.
Franzen, S.; Boxer, S. G. Manipulation of Electron Transfer Reaction Rates with Applied Electric Fields—Application to Long-Distance Charge Recombination in Photosynthetic Reaction Centers.
Iwaki, M.; Itoh, S. Function of Quinones and Quinoids in Green-Plant Photosystem-1 Reaction Center.
McLendon, G.; Hickey, D.; Berghuis, A.; Sherman, F.; Brayer, G. Effects of Reaction Free Energy in Biological Electron Transfer in Vitro and in Vivo.
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Natan, M. J.; Baxter, W. W.; Kuila, D.; Gingrich, D. J.; Martin, G. S.; Hoffman, B. M. Long Range Electron Transfer in Mixed-Metal Hemoglobin Hybrids.
Ohno, T.; Nozaki, K.; Ikeda, N.; Haga, M. Electron Transfer, Energy Transfer, and Excited State Annihilation in Binuclear Compounds of Ruthenium(II).
Isied, S. S. Electron Transfer Across Model Polypeptide and Protein Bridging Ligands—Distance Dependence, Pathways, and Protein Conformational States.
Zhang, X.; Kozik, M.; Sutin, N.; Winkler, J. R. Solvent Reorganization Energetics and Dynamics in Charge Transfer Processes of Transition Metal Complexes.
Miller, J. R. Puzzles of Electron Transfer.

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Volume I. *Top. Curr. Chem.* 1991, *156*.
Roth, H. D. A Brief History of Photoinduced Electron Transfer and Related Reactions.
Kavarnos, G. J. Fundamental Concepts of Photoinduced Electron Transfer.
Saeva, F. D. Photoinduced Electron Transfer (PET) Bond Cleavage Reactions.
Krogh, E.; Wan, P. Photoinduced Electron Transfer of Carbanions and Carbocations.
Lopez, L. Photoinduced Electron Transfer Oxygenations.
Timpe, H. J. Photoinduced Electron Transfer Polymerization.
Eaton, D. F. Electron Transfer Processes in Imaging.

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Vogler, A.; Kunkely, H. Photochemistry of Transition Metal Complexes Induced by Outer-Sphere Charge Transfer Excitation.
Balzani, V.; Barigelletti, F.; De Cola, L. Metal Complexes as Light Absorption and Light Emission Sensitizers.
Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. Photoinduced Electron and Energy Transfer in Polynuclear Complexes.
Billing, R.; Rehorek, D.; Henning, H. Photoinduced Electron Transfer in Ion Pairs.
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Fox, M. A. Photoinduced Electron Transfer in Arranged Media.
Gust, D.; Moore, T. A. Photosynthetic Model Systems.
Willner, I.; Willner, B. Artificial Photosynthetic Model Systems Using Light-Induced Electron Transfer Reactions in Catalytic and Biocatalytic Assemblies.
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Suppan, P. The Marcus Inverted Region.
Roth, H. D. Structure and Reactivity of Organic Radical Cations.

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Fox, M. A. Photoinduced Electron Transfer of Irradiated Semiconductor Surfaces.
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Schuster, G. B. Electron Transfer Reactions Followed By Rapid Bond Cleavage: Intra Ion Pair Electron Transfer of Photoexcited Cyanine Borates.
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Fukuzumi, S. Mechanisms and Catalysis in Electron Transfer Chemistry of Redox Coenzyme Analogues.
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Jones, G., II. Photoinduced Electron Transfer in Dye-Polymer Conjugates.
Guengerich, P.; Macdonald, T. L. Sequential Electron Transfer in Oxidation Reactions Catalyzed by Cytochrome P-450 Enzymes.
Nelsen, S. F. Inner Shell Relaxation Effects on Electron Transfer Reactions of Amino Centered Systems.
Saveant, J.-M. Outer Sphere and Inner Sphere Electron Transfers in Organic and Organometallic Chemistry.
Gust, D. Multistep Electron Transfer Strategies for Artificial Photosynthesis.

Even this broad range of themes cannot do justice to the topic. May this issue serve to whet the appetite of the chemist hungering for insight into a common basis of his/her discipline!

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