

# Chemical Reviews

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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.; Desfrancois, 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.

- Wilkinson, F. Competition between Energy and Electron Transfer.
- Mauzerall, D. C. Circumventing Reverse Electron Transfer.
- Jones, G., II. Photochemistry and Photophysics of Organic Charge Transfer Complexes.
- Haas, Y.; Anner, O. Jet-Cooled Exciplexes.
- Calef, D. F. Theoretical Treatments of Solvent Effects.
- Eriksen, J. In-situ Generated Intermediates.
- Chanon, M. Ebersson, L. Photochemistry of Homogeneous and Heterogeneous Chemical Gears Involving Electron Transfer Catalysis: Chains, Catalysts, and Sensitization. Relations of Electrochemistry, Synthetic Applications, and Mechanistic Basis for Selectivity.
- Part B. *Experimental Techniques and Medium Effects*
- Delaire, J. A.; Faure, J. Laser Spectroscopic Methods.
- Waltz, W. L. Pulse Radiolysis.
- Neta, P.; Harriman, A. Pulse Radiolysis Studies of Organic Electron Transfer.
- Boxer, S. G.; Goldstein, R. A.; Franzen, S. The Use of Magnetic and Electric Fields to Probe Electron Transfer Reactions.
- Julliard, M. Classical Methods.
- Brus, L. Electron Transfer Reactions Studied via Time-Resolved Resonance Raman Spectroscopy.
- Kevan, L. Electron Spin Resonance: CW and Pulsed Methods and Applications to Photoionization in Micelles and Vesicles.
- Baggett, J. E. The Temperature Dependence of Photoinduced Electron Transfer Reactions.
- Langford, C. H.; Moralejo, C. Wavelength Dependence of Photochemical Electron Transfer Reactions.
- Kirk, A. D. Pressure as a Variable in Studies of Electron Transfer Processes.
- Santamaria, J. Solvent and Salt Effects.
- Baral, S.; Fendler, J. H. Photoinduced Electron Transfers in Membrane Mimetic Systems.
- Nakabayashi, S.; Kawai, T. Electron Transfer at Interfaces.
- Rabani, J. Polyelectrolytes.
- Part C. *Photoinduced Electron Transfer Reactions. Organic Substrates*
- Lewis, F. D. Carbon-Carbon Multiple Bonds.
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- Albini, A.; Sulpizio, S. Aromatics.
- Lablache-Combier, A. Heteroaromatics.
- Hoshino, M.; Shizuka, H. Photoinduced Electron Transfer Reactions of Aromatic Carbonyl and Related Compounds.
- Mariano, P. S. Electron Transfer Photochemistry of Iminium Cations.
- Pienta, N. J. Amines, Thiols, and Thioethers: Heteroatomic Electron Donors.
- Bowman, W. R. Photoinduced Nucleophilic Substitution at  $sp^3$ -Carbon.
- Ci, X.; Whitten, D. G. Light-Induced Redox Reactions of Dyes, Metal Complexes, and Amines: One- vs. Two-Electron Transfer Reactions and C-C Bond Cleavage Processes.
- Fukuzumi, S.; Tanaka, T. NAD(P)H, NAD(P)<sup>+</sup>, and Analogues.
- Fukuzumi, S.; Tanaka, T. Flavins and Deazaflavins.
- Part D. *Photoinduced Electron Transfer Reactions: Inorganic Substrates and Applications*
- Fox, M. A. Activation of Oxygen by Photoinduced Electron Transfer.
- Macke, H. R.; Williams, A. F. Dioxygen-Transition Metal Complexes.
- Serpone, N. Photoinduced Electron Transfer in Hexacoordinate Inorganic Complexes.
- Balzani, V.; Scandola, F. Photoinduced Electron Transfer in Coordination Compounds: Ion-Pairs and Supramolecular Systems.
- Vogler, A. Photochemical Reactions of Transition Metal Complexes Induced by Intramolecular Electron Transfer between Weakly Coupled Redox Centers.
- Giannotti, C.; Gaspard, S.; Krausz, P. Photoinduced Electron Transfer in Organometallic Transition Metal Complexes.
- Pichat, P.; Fox, M. A. Photocatalysis on Semiconductors.
- Connolly, J. S.; Bolton, J. R. Intramolecular Electron Transfer: History and Some Implications for Artificial Photosynthesis.
- Grätzel, M. Solar Energy Harvesting.
- Shirota, Y. Polymerizations Induced by Photochemical Electron Transfer.
- Alfimov, M. V.; Sazhnikov, V. A. Information Management and Storage.
- Schue, F.; Giral, L.; Montginoul, C.; Serre, B. State of the Art in Resists Used in Microlithography.
- Paillous, N.; Comtat, M. Electron Transfer in Drug-Induced Photosensitization Processes.
- Electron Transfer in Biology and the Solid State. Inorganic Compounds with Unusual Properties.* Johnson, M. K., King, R. B., Kurtz, D. M., Jr., Kutal, C., Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990.
- Williams, R. J. P. Overview of Biological Electron Transfer.
- Reimers, J. R.; Hush, N. S. Formalism for Electron Transfer and Energy Transfer in Bridged Systems.
- Sutin, N.; Brunschwig, B. S. Some Aspects of Electron Transfer in Biological Systems.
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- Dixon, D. W.; Hong, X. Electrostatic, Steric, and Reorganizational Control of Electron Self-Exchange in Cytochromes.
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- Lewis, N. A.; Taveras, D. V. High-Pressure Studies

- of Long-Range Electron-Transfer Reactions in Solution.
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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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