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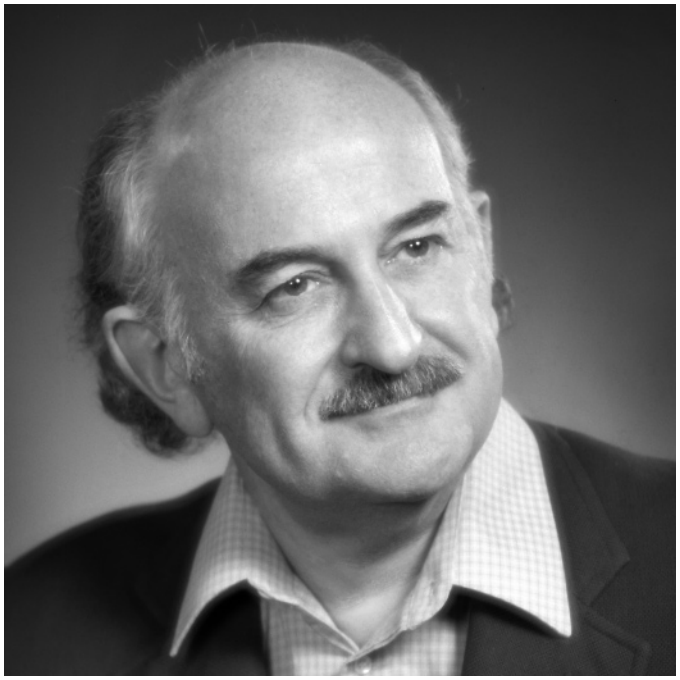

Norman Sutin: Contributions to Chemistry

We are pleased to be the guest editors for this special issue of *The Journal of Physical Chemistry B* honoring Norman Sutin and the impact he has had on the field of charge-transfer chemistry. We thank the many colleagues and friends of Norman who have come forward with contributions to the Festschrift. The variety and quality of their science is a testament to Norman's influence. We also thank Dr. Prashant Kamat, the Editor in charge of this special issue, for his help.

Norman's work initially focused on understanding the fundamental mechanism of electron-transfer reactions. He was an early leader in applying and extending the ideas of Marcus and Hush to these reactions. While his contributions have often centered on outer-sphere electron-transfer reactions, in which interaction between the reactants is small, he has also addressed strongly interacting systems, the rates of high-spin low-spin reactions, excited-state dynamics, and proton-transfer reactions. He has stressed the importance of the reorganization energy in understanding electron-transfer reactions and has shown how to disentangle the contributions of nonadiabaticity and nuclear reorganization on the rates of these reactions. He has developed the methods that are used to distinguish between energy- and charge-transfer mechanisms. Norman's methods have also found wide application in the understanding of mixed-valence systems, biological electron transfer, and, recently, interfacial charge transfer.

Norman's study of fast reactions resulted in the development and improvement of experimental techniques on increasingly faster time scales. He has improved stopped-flow methods (ms regime), invented with George Flynn the laser temperature-jump technique (μs regime), and pioneered the use of laser flash photolysis (ns regime) in the study of inorganic reactions.

Norman's studies of excited-state electron-transfer reactions have provided many of the basic ideas needed for solar energy conversion. Norman was the first to show that the excited state of tris(bipyridine)ruthenium(II) was oxidized in reactions with cobalt(III) and ruthenium(III) complexes. His work initiated the use of transition-metal complexes in the "fixing" of photons into energetic chemical species. He has played a leading role in the development of schemes to use solar energy to split water or reduce carbon dioxide. He was one of the first to study

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methods of sensitizing wide-band-gap semiconductors with a transition-metal dye such as tris(bipyridine)ruthenium(II), work that helped lead to the development of dye-sensitized solar cells.

Contributions to this issue reflect the breadth of Norman's interests. While Norman primarily used transition-metal complexes to study the problems of charge transfer, his work has impacted both physical-inorganic and -organic chemistry. His many review articles have taught a large group of chemists the importance of electron-transfer reactions, and his work has elucidated the use of his semiclassical two-state model to gain a detailed understanding of charge-transfer reactions.

Norman's measured, yet passionate, approach to understanding reactivity has resulted in a large community of scientists who have collaborated with him and/or benefited from his writings. Everyone who knows him appreciates his friendly manner, his scientific integrity, and his concern for people. Working closely with Norman has been a great privilege for many of us.

Bruce S. Brunschwig
Carol Creutz

Norman Sutin: A Personal Tribute

It is a pleasure to participate in this issue honoring a long-time friend and colleague, Norman Sutin. In the early days of electron transfer almost 50 years ago, Norman pioneered the application of fast stopped-flow techniques to the study of electron-transfer reactions, determining the effect of the driving force, $-\Delta G°$, and reorganization energies on the rates of electron-transfer reactions, and extending Henry Taube's inner-sphere atom-transfer mechanism to fast reactions. Later, Norman initiated the use of "Rubpy", tris(2,2′-bipyridine)ruthenium(II), to studies of photoinduced electron transfer by showing that its excited state can be quenched by electron transfer. Today, "Rubpy" is a central player in the quest to construct solar conversion devices to split water, and a Google search on tris(2,2′-bipyridine)ruthenium(II) returns almost 100,000 hits!

For me personally, those were heady days when at the invitation of another pioneer in isotope exchange electron transfers, Dick Dodson, I often traveled by train from "Brooklyn Poly" where I was teaching to the Brookhaven National Laboratory on Long Island.

On this occasion of honoring Norman, I recall some of those early events. I remember vividly the excitement during a conversation with Norman in about 1962. I mentioned to him some of the predictions I had made in an article on electron transfer. They included the cross-relation, the dependence of the reaction rate on the driving force of the reaction, and the "inverted effect". The first of these related the rate constants of cross-reactions to those of the two relevant self-exchange reactions. Because of his studies of fast electron transfers, Norman knew of six sets of data to test the relation. The two of us could hardly contain our enthusiasm and excitement when the successive comparisons of experiment and theory showed encouraging agreement. About the same time, Norman also studied the dependence of the electron-transfer rate on $\Delta G°$ with his fast reaction methods and provided the first confirmation of the theoretically predicted slope.

Another example is in the extension of the cross-relation. Originally, it was derived for electron-transfer reactions, but Norman had also studied experimentally redox reactions that proceed by atom transfers. When he applied the cross-relation to examples of these reactions, it worked! Of course, we knew that the formalism was intended for electron transfers with their peculiarities such as intersecting reactant's and product's parabolas. Norman's success prompted me to develop an approach to these reactions involving the rupture and formation of chemical bonds.

Another experience was the interaction that Norman and I had preparing an article that appeared in 1985 in *Biochimica et Biophysica Acta*, a review of electron-transfer reactions with applications to biological systems. It was a review coming at the right time, when applications to biological electron transfer were becoming common. It subsequently received more than 4,000 citations, which impressed and certainly surprised both Norman and me. Norman and I collaborated on a number of other topics, such as electron transfer with negative activation energy. I recall the pleasure we had in seeing how a negative activation energy could result from the 1956 electron-transfer theory.

Norman has been daring in his approach to science. His modeling of nuclear-tunneling contributions to the rates of electron transfer was begun in the early 1960s. His studies of the rates of oxidation of the biologically important substrates, such as ferro-haemoglobin and ferro-cytochrome *c*, by small inorganic transition-metal complexes in the early 1960s showed his recognition of the importance of electron transfer in biological systems. Norman foresaw the need for faster methods to study chemical kinetics. He developed a laser temperature-jump instrument that was 3 orders of magnitude faster than other methods available at the time and was a pioneer in the use of flash photolysis to study photoinitiated electron-transfer reactions. Norman was among the first to study the sensitization of a TiO_2 semiconductor by a Rubpy type complex in the 1970s. He built an early example of a liquid junction solar cell and studied systems that were capable of photochemically reducing water. This latter work has continued to grow in importance as we face the problems of global warming and a reduced supply of oil.

We in the field of electron transfers owe a tremendous debt to Norman, not only for his pioneering developments but also for his high intellectual standards, his good humor, and his attitude that have contributed to making research in our field such a pleasure.

R. A. Marcus