

Physical organic chemistry. Electron transfer chemistry. Molecular electrochemistry

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Biography: Jean-Michel Savéant was born in 1933. He received his education in the Ecole Normale Supérieure in Paris, where he became the Vice-Director of the Chemistry Department before moving to the University Denis Diderot (Paris 7) as a Professor in 1971. He is, since 1985, Directeur de Recherche au Centre National de la Recherche Scientifique. In 1988–1989 he was a distinguished Fairchild Scholar at the California Institute of Technology. His current research interests involve all aspects of molecular electrochemistry as well as mechanisms and reactivity in electron transfer chemistry.

Forecasting the future of a scientific field is by nature more of a subjective exercise than of a scientific task. How the boundaries between the various scientific fields became established was not of designed purpose. How they could be displaced or erased is likewise unlikely to be the fruit of a rational plan. As it stands now, physical organic chemistry is obviously related to many other fields of chemistry. It is thus tempting to dynamite the barriers separating these fields for the sake of a more rapid and reliable progress of knowledge. Progressively one may thus rediscover the unity of chemistry and ultimately the unity of the physical sciences. It seems more realistic to prefer evolution to revolution, to start with what we have and try to encourage what seems promising among the ongoing trends.

Why organic? Why physical? The heart of physical organic chemistry is and should remain, in my opinion, the understanding of chemical reactivity. Because their structure can be finely tuned, organic molecules have provided and continue to provide a privileged manifold for investigating the relationships between molecular structure and reactivity. Many of the techniques and concepts thus employed may be extended to transition metal chemistry and to the chemistry of small inorganic molecules, albeit not always in a straightforward manner. Organometallic systems thus appear as a natural bridge between these various areas. Therefore, what is potentially most important in “organic” is the implicit reference to molecular aspects rather than a strict reference to organic compounds. This extends to supramolecular assemblies since they are built from molecules, even if it is true that the comprehension of their cooperative properties is an important part of the story.

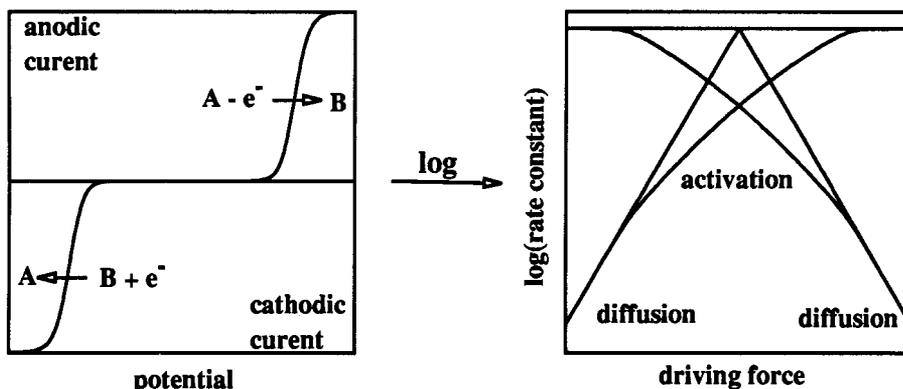
“Physical” sounds as a fierce declaration of rationality (the discourse of chemistry should not be confounded with the discourse of a cookbook). Simultaneously, it carries with it the long-standing complex of inferiority of chemistry towards physics (rationality can come only from the outside of chemistry, namely from physics). Many years ago, one of my fellow students used to tell me “why do you care for chemistry? Chemistry is a closed problem; don't we have the Schrödinger equation?” Actually, the ambivalent status of theory in chemistry has factual roots. Because the pressure to produce and explain “useful” chemistry goes through the whole chemists' community and reaches even the most theoretically oriented of them, because the chemical phenomena are complex and “useful” chemistry cannot wait, a huge mass of empirical observations is produced which educates the chemist “intuition” before a rationally organized explanation is ready. Hence the success of empirical relationships (Hammett and other free energy relationships). Even if they do not uncover the physical (again!) roots of the phenomena, they have the value of putting order in the empirical observations and thus to serve both as starting points and goals for further theoretical developments. Designing an experiment in order to verify a theory is certainly not as common an approach as in physics. However, there is hope for progress along these lines thanks to the availability of more and more powerful experimental techniques and theoretical tools. Such developments seem worth encouraging even if the inherent complexity of chemical reactions is likely to limit their success to semi-quantitative predictions. Even the

mere identification of the key structural and environmental factors that govern the dynamics of the various types of chemical reactions and the ensuing establishment of reactivity guidelines is a worthwhile goal. Purposely designed molecules and experiments may then serve to illustrate the pertinence of the parameters thus unraveled.

Investigation of chemical reactivity in physical organic chemistry has long been the realm of electron pair transfer reactions. However, *single electron transfer* reactions have attracted increasing attention over the past twenty years. This interest has been concerned with outer-sphere reactions but also with more complex processes where electron transfer is coupled concertedly or sequentially with bond breaking or bond formation. Much is still to be discovered in this field both in terms of mechanisms and reactivity. However, the prognosis of future advances seems rather favorable both from a theoretical and an experimental standpoint. As compared to electron pair transfers, the dynamics of chemical changes triggered by single electron transfer seems indeed more amenable to the establishment of activation - driving force relationships that do not merely derive from empirical observations but are based on the identification of pertinent reactivity-governing factors as in Marcus theory of outer-sphere electron transfer reactions. It also seems important to parallel and/or to inspire these attempts by quantum chemical calculations, even if these are performed on such simplified model systems as may prove necessary for obtaining reliable results. From an experimental point of view, a favorable factor should be the possibility of approaching the same reaction from various angles (photochemistry, electrochemistry, pulse radiolysis). In this respect similarities and differences in the results are equally inspiring. Single electron transfer chemistry is also a privileged domain for attempting to apply the same reactivity concepts to organic, organometallic, and inorganic systems. Reactions at the crossroads of electron pair transfer and single electron transfer chemistry, where small changes in structure may trigger the passage from one reaction path to the other, are of particular interest for a better understanding of both types of reactivity and of the relationship between them. A related question deals with the nature of electron pair transfer reactions; are they better described as such or as inner-sphere single electron transfer processes? It should also be borne in mind that the unraveling of mechanism and reactivity problems in single electron transfer chemistry may have important consequences in other domains such as synthesis, catalysis, radical chemistry, and biochemistry.

Let me close with a few (subjective) remarks on the role of *electrochemistry* in physical organic chemistry. Electrochemists are certainly happy that electrochemical data are increasingly used in the field and that more and more non-electrochemist users arrange to gather these data themselves by means of cyclic voltammetry and a few other related techniques. They however feel somewhat frustrated to see that, in a large number of cases, the determination of standard potentials is the exclusive goal. In this respect, reversible cyclic voltammograms are among the most cherished hopes and electrochemical kinetics are at best regarded as an unpleasant source of trouble. In fact, electrochemical kinetics is the source of precious mechanistic and reactivity information that may be used far beyond the boundaries of electrochemistry. Just a few examples.

The theories of outer-sphere and dissociative electron transfers apply to both electrochemical and homogeneous reactions. Testing their electrochemical version has several advantages. It should be realized in this connection that a cyclic voltammogram or a rotating electrode voltammogram is the equivalent of a Brønsted plot, as illustrated below.



The continuous lines drawn in the figure are an almost exact representation of reality since the driving force can be changed, through the electrode potential, almost continuously with a precision of the order of

1 meV. The current is also a particularly convenient measure of the rate constant, making the automatic recording of the Brønsted plot an easy task (compared with the construction of a conventional Brønsted plot with a series of different reagents reacting with the substrate). Another interesting feature is that the diffusion rate can be easily varied, just by changing the scan rate or the rotation rate. Detailed analyses of Brønsted plots thus obtained, such as examination of the variation of the symmetry factor with the driving force, are much easier and much more precise than with conventional Brønsted plots.

More complex mechanisms can also be analyzed by similar techniques, allowing the characterization of the reactions that are triggered by the injection of electrons into (or removal from) a molecule. Probably the main mental obstacle to the diffusion of such approaches to physical organic chemistry resides in the fact that the conventional homogeneous kinetics must be replaced by heterogeneous kinetics taking account of the diffusion of the various species toward or from the electrode surface. Thus, besides the time variable, a space variable comes into play. There is, however, nothing insuperable in this additional complexity. The necessary physics and algebra have been worked out, simulation packages for PCs are available, and instrumentation is neither very sophisticated nor very expensive. Probably the best way to overcome these obstacles in the future would be to inject a small section devoted to molecular electrochemistry into the undergraduate physical chemistry courses. It may be noted, *en passant*, that electrochemical kinetic concepts may be easily adapted to the resolution of kinetic problems in non-electrochemical heterogeneous reactions and also in reactions that are apparently homogeneous but are so fast that they actually occur during the mixing of reactants, an important area that has been rather neglected so far.

The vast possibilities offered by indirect (mediated) electrochemistry should also be more systematically exploited. A reactant is generated electrochemically and its homogeneous reaction with the substrate can be monitored by the ensuing variation of the current. The reactions of single electrons as well as of electron pair donors or acceptors can be followed by this method. This *in situ* generation allows the investigation of very reactive species, the only limit being that they should react with the substrate faster than they react with any other molecule present in the solution.

Instrumental combination of electrochemistry and photochemistry seems promising for determining the properties of transient species such as radicals, carbenes, *etc.* (photolytic generation + electrochemical detection, electron photoinjection + electrochemical detection). The use of electrochemically generated chemiluminescence as a diagnostic tool has also many potential applications.

Last, but not least, electrodes, particularly ultramicroelectrodes, chemically derivatized or coated with self-assembling molecules appear as a natural means to express electrically the potential properties of supramolecular engineered systems. Also, the templating effect of the electrode surface can be exploited to construct, using immunological or similar interactions, spatially ordered catalytic enzymatic systems of controlled activity. Enzymatic catalysis can thus be easily related to the current flowing through the electrode with possible application to biosensors or preparative biotechnologies.