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A Pioneering Career in Electrochemistry: Jean-Michel Savéant

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ABSTRACT: Prof. Jean-Michel Savéant sadly passed on August 16 2020. We would like to honor his memory, his tremendous contribution to electrochemistry and its use for a general understanding of the laws of physical chemistry. In this review, we highlight his decisive role in the foundation of molecular electrochemistry. We also present his major achievements in the field of molecular and biomolecular catalysis. Finally, we review his unique contribution to dissociative electron transfers and to the electrochemical approach of proton-coupled electron transfers. This shows how various concepts rigorously established and experimentally validated assemble to each other to enlighten complex systems.

Introduction

Molecular electrochemistry is a “segment of electrochemistry where attention is primarily focused on the molecular changes brought about by electron transfer to or from an electrode.” Thus defined, it is immediately evident that molecular electrochemistry can be an extraordinary tool to investigate many aspects of molecular reactivity and irrigates many fields of chemistry and biochemistry. Prof. J-M. Savéant, who sadly passed on August 16 2020 dedicated his long career to develop, conceptualize and use molecular electrochemistry. It is not possible to mention all contributions of J-M. Savéant who published almost 500 papers. We will thus focus on a few salient contributions with particular emphasis to the field of catalysis.

Born in Brittany in 1933, Jean-Michel Savéant received his education at Ecole Normale Supérieure in Paris where he was laureate of the “Agregation de Sciences Physiques”. After a pre-doctoral stay at the Istituto di Chimica Fisica dell' Università di Padova in 1959, where he met Prof. Elio Vianello, he served two years (1960-62) as Officer in the French Marine for his Military Service. He then returned to Ecole Normale Supérieure where he received his Doctorat-ès-Sciences Physiques (PhD) in 1966. He was then Agrégé-Préparateur and the Vice-Director of the Laboratoire de Chimie of the same school, leading an electrochemistry group. In 1971 he moved with his group to the newly created Université Paris 7 (now Université de Paris) where he established the Laboratoire d'Electrochimie later named Laboratoire d'Electrochimie Moléculaire in 1988. He was professor until 1985 when he became Directeur de Recherche at CNRS and then kept this position as a CNRS emeritus. Recognized as a great scientist, he was elected both at the French Académie des Sciences (2000) and as a Foreign Associate of the National Academy of Science of the USA (2001). With his strong personality, J-M. Savéant was often both admired and feared for his intransigence toward scientific rigor. Along his career, he developed strong interaction with scientists across the world, in particular in Italy a country that he was in love with and admires the culture and languages, being able to speak fluently Italian as well as Venetian dialect. He also developed

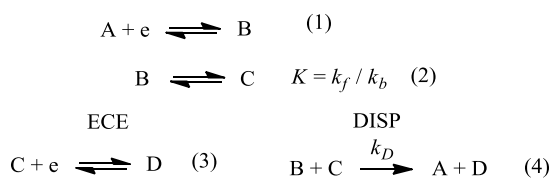
scientific and friendly relationships in the US, in particular with Fred Anson at Caltech where he was invited Professor in 1988-89 as a Sherman Fairchild Distinguished Scholar, and with Allen J. Bard at the University of Texas who was on sabbatical in J-M Savéant's lab in 1973. He received many awards among them the Bruno Beyer Award of the Royal Australian Chemistry Institute (2005), ECS Organic and Biological Electrochemistry Division Manuel M. Baizer Award (2002), the ECS Olin Palladium Award (1993), and Faraday Medal of the Royal Chemical Society (1983). He was Oskar K. Rice Distinguished Lecturer at the University of North Carolina, Chapel Hill (1995), Nelson Leonard Distinguished Lecturer at the University of Illinois (1999), and George Fisher Baker Lecturer at Cornell University (2002). This was the occasion to write his book “Elements of Molecular and Biomolecular Electrochemistry”.¹

Foundation of Molecular Electrochemistry

J-M. Savéant started his career at a time where analytical electrochemistry was dominated by aqueous electrochemistry and polarography as the most popular analytical technique. The development of a new technique, *e.g.* cyclic voltammetry (CV), was at its infancy but he quickly realized that it could be a very powerful tool to study both interfacial electron transfers and chemical reactions associated to/triggered by electron transfer. At the same time, electrochemistry in organic solvents got more common, thus giving rise to new opportunities to use electrochemistry for studying organic reactions and/or perform organic electrochemistry, *i.e.* organic transformations triggered by interfacial electron transfer. However, there were at least two requirements for the development of the use of cyclic voltammetry as a technique to investigate reactions: one was the development of suitable instrumentation, *i.e.* potentiostat with fast enough operational amplifiers, and the other was the development of a formal framework to analyze CVs. The contribution of J-M. Savéant in the later is now widely recognized and it was actually acknowledged from the very beginning (together with his collaborator and dear friend Elio Vianello²) as indicated by the following quotation of Nicholson and Shain in their famous 1964 Anal. Chem. paper (Theory of Stationary Electrode Polar-

ography): “Savéant and Vianello developed the theory for the catalytic mechanism, the preceding chemical reaction, and also have discussed the case involving a very rapid reaction following the charge transfer”.³ From their fruitful collaboration initiated during the pre-doctoral stay of J-M Savéant in Padova, J-M. Savéant and E. Vianello published in 1967 a seminal paper on the general theory for the calculation of voltammetric wave corresponding to a chemical reaction of any order, preceding, following or parallel to an electron transfer.⁴ It can be considered as an important piece in the foundation of molecular electrochemistry. At the same time, experimental studies were undergone by the first students mentored by J-M. Savéant, Claude Andrieux and Louis Nadjo,^{5,6} and it appeared that considering mechanisms involving more than one electron transfer was also mandatory. Then the famous **ECE/DISP** mechanism (Scheme 1) was on stage and we will shed light on it as an emblematic achievement. Taking the example of a reduction of a neutral organic molecule, injection of an electron makes it more basic or nucleophile and the electron transfer event is often followed by an irreversible chemical reaction, for example protonation or expulsion of a nucleophile, leading to a neutral radical usually more reducible than the starting molecule, then triggering a second electron transfer. Such an overall bi-electronic irreversible process may follow several pathways that are worth investigating in particular to predict possible branching processes. One important question is whether the second electron is transferred directly from the electrode (ECE) or from the solution species, namely the singly reduced species *via* a disproportionation reaction (DISP) as sketched on Scheme 1. Investigation of the ECE/DISP dichotomy by J-M Savéant started in 1968 with a first theoretical analysis⁷ and experimental illustration.⁸ It reached its climax in 1977 and 1979 with the publication of the general resolution of the problem.^{9,10} Notably, this decade journey involved several important students and then collaborators of J-M. Savéant, C. Andrieux,¹¹ L. Nadjo,¹² and the decisive contribution of Christian Amatore.^{9,10}

Scheme 1. ECE–DISP mechanisms



DISP1: (2) rate determining step
 DISP2: (2) at equilibrium, (4) rate determining step

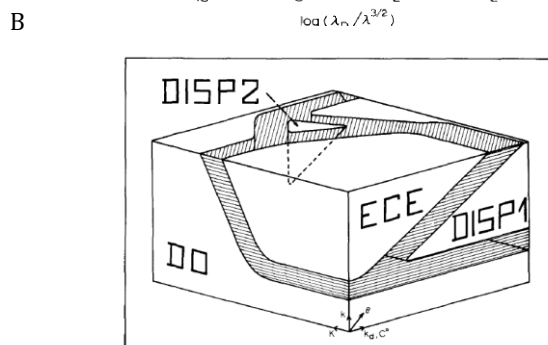
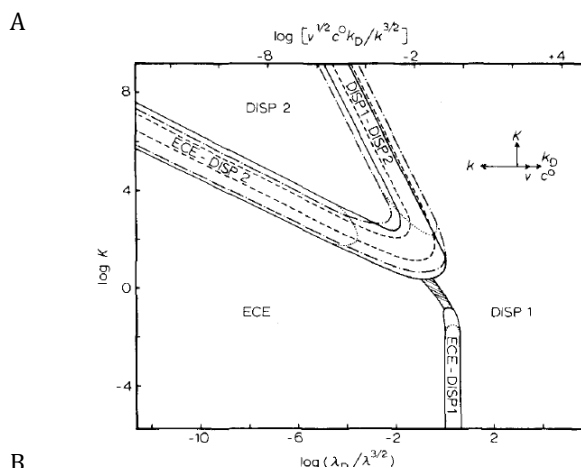
This ECE/DISP problem illustrates the methodology put forward by J-M. Savéant to study mechanisms with molecular electrochemistry: (i) set the diffusion-reaction systems, (ii) use a dimensionless formulation to derive the minimal number of governing parameters, (iii) explore limiting cases corresponding to extreme values of the governing parameters, and (iv) draw zone diagrams showing how the system, and hence the CV and its characteristics (shape, intensity, position), is modified upon varying the experimental parameters (scan rate, concentrations, etc.). Finally, (v) illustrative systems are studied and reported.

In the specific case of the ECE/DISP competition, three mechanisms are involved: ECE, DISP₁ and DISP₂ (Scheme 1). Considering “pure kinetics” conditions, *i.e.* when a stationary state is obtained for intermediates due to mutual compensation of diffusion and chemical reaction, the system is governed by two parameters, $K = k_f / k_b$ the equilibrium constant of the first chemical step and

$$\left(\frac{RT}{Fv} k_D C^0 \right) \left[\frac{Fv}{RT(k_f + k_b)} \right]^{3/2}$$

a competition parameter (F

is the Faraday, T the temperature, R the gas constant, v the scan rate and C^0 the bulk concentration of the substrate A). The resulting zone diagram is shown in Figure 1A, revealing three distinct zones where only one mechanism is dominant, as well as transitions zones where two mechanisms are in competition, and a general zone for which all three mechanisms are operatives. The effect of the various parameters (scan rate v , substrate concentration C^0 , equilibrium constant K , rate constant k_D and $k = k_f + k_b$) are anticipated *via* the arrows in the upper right compass. Boundaries between zones are determined using criteria on either peak potential (E_p), E_p vs. $\log v$ slope, or peak width. Whereas the effect of rate constants and substrate concentration is intuitively easily predicted from the observation that the first chemical step is first order (large k leads to C being produced close to the electrode surface and hence reduced by the electrode), disproportionation is second order (favored for high concentration of substrate) and so the effect of scan rate is difficult to anticipate. The theoretical analysis shows that low scan rate favors the ECE mechanism.



C

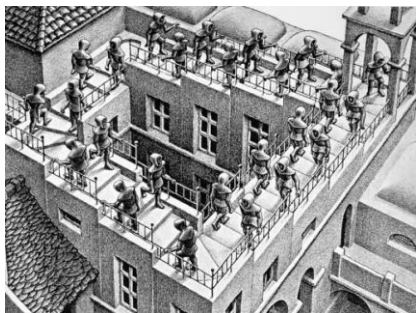


Figure 1. (A) ECE-DISP zone diagram adapted from ref. 9. (B) ECE-DISP 3D zone diagram adapted from ref. 10. (C) Escher drawing viewed as a “zone diagram cartoon”.

The general case, *i.e.* removing the “pure kinetics” conditions, involves three governing parameters, the thermodynamic constant K , and both kinetic parameters $\lambda_D = k_D C^0 / (RT/Fv)$ and $\lambda = k / (RT/Fv)$ leading to the three-dimensional zone diagram shown on Figure 1B. These formal analyses were used to study experimental systems based on organic molecules by the group of J.-M. Savéant,¹³ but also others,¹⁴ and it was shown to apply to transition metal complexes underscoring the generality of the concepts.¹⁵ Note that the use of zone diagrams is very convenient in mechanism analysis although it is often viewed by neophytes as confusing labyrinth as cartooned on Figure 1C.

As already mentioned, the development of cyclic voltammetry in organic solvents was an opportunity to investigate in details *outersphere interfacial electron transfers* and test predictions of the Marcus-Hush theory developed in the late 60's.¹⁶ One of the peculiar features of ET theories is the prediction that the transfer coefficient depends on the potential. In other words, the nonlinear character of the kinetic law should be revealed if current-potential curves can be analyzed over large range of potentials. This was made possible *via* the use of the **convolution technique**.^{17,18,19,20} The basis of the method is simply a mathematical manipulation of the raw data obtained from CV using the function $1/\sqrt{\pi t}$ characteristic of transient linear semi-infinite diffusion.²¹ This allows calculating the convolution integral from the experimental data. It is of particular interest to extract the kinetic law for a simple electron transfer process without any assumption on the form of the rate law following the procedure described in ref. 22. One important achievement of the use of convolution on CV data was the demonstration that the transfer coefficient varies linearly with potential in the case of reduction of *tert*-nitrobutane,²³ as predicted by the Marcus-Hush theory (Figure 2).¹⁶

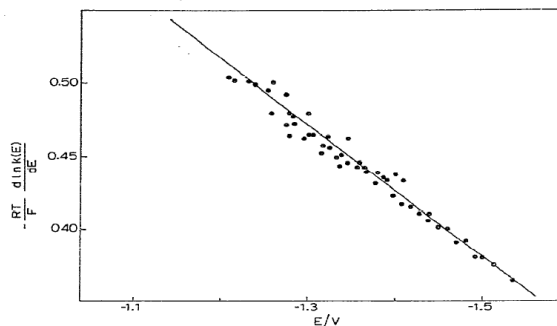


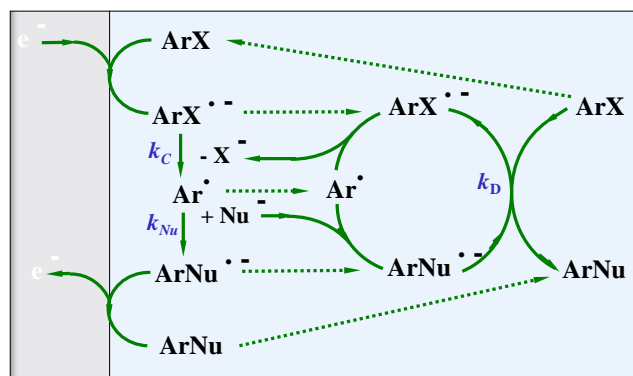
Figure 2. *Tert*-nitrobutane in DMF. $-(RT/F) \frac{d \ln k(E)}{dE}$ as a function of the electrode potential E referred to Ag/AgI reference electrode ($k(E)$ is the electron transfer rate constant). Adapted from ref. 23.

Convolution potential sweep voltammetry was used up to scan rate in the range of kV/s to study electrochemical kinetics.²⁴ Technical limitations had to be overcome to reach such high scan rates at that time. While the emergence of CV as a popular technique in the 60's was partly due to the availability of amplifiers allowing the development of potentiostats, limitations resulting from the bandpass of the amplifiers and from the influence of ohmic drop effect on the faradaic current were still a problem at high scan rates. J.-M. Savéant's contribution in this area of **instrumentation** is noticeable through the early development of a potentiostat enabling ohmic drop compensation *via* positive feedback.²⁵ Later he was also involved in the development of instrumentation dedicated to fast voltammetry at ultramicroelectrodes²⁶ as well as in the use of a more specific technique: laser pulse photoinjection of electrons from metal electrodes and its application to study organic radicals in aprotic solvents.²⁷ Although J.-M. Savéant's contribution in the formal description of mechanism analysis is particularly noticeable, his interest for instrumentation was constant as he was convinced that solid experimental data are a pre-request for mechanism understanding. Hence, he was always warning students of possible misinterpretation if using a technique without being aware of instrumentation artifacts as was the case for the use of second-harmonic ac voltammetry.²⁸

Besides investigation of electrochemical reactions, analytical electrochemical techniques, such as cyclic voltammetry, can be used to trigger non-electrochemical reactions. In such a case, the electrode or more precisely electrons are catalysts. This field of **electron catalyzed chemical reactions** is currently experiencing a renewed large interest,²⁹ but it was already investigated in the 80's.³⁰ A prominent example was the detailed study of “aromatic $S_{RN}1$ ” substitution reactions.³¹ Not only did J.-M. Savéant show that these reactions can be triggered by an electrode but, following his typical approach, he did formalized the problem and used typical examples to decipher the mechanism. Substitution of a halide ion or other leaving groups by a nucleophile at an aromatic carbon does not occur spontaneously. It requires induction by an electron or by light. A typical example is the reaction of 4-bromobenzophenone

with thiophenolate triggered at an electrode polarized at a potential allowing reduction of the substrate ArX. Only 0.2 electrons per substrate is consumed while the conversion yield is 80%. This can be rationalized by the mechanism depicted in Scheme 2. Cyclic voltammetry appeared as a useful tool to study such processes. The critical bottleneck of the mechanism is the fate of the radical Ar• which can either be reduced (ECE/DISP mechanism), leading to a two-electron CV wave, or react with the nucleophile to produce the anion radical which can then oxidize at the electrode or diffuse in solution to enter a loop consuming the substrate, and thereby to a zero electron wave.³²

Scheme 2. Electrochemically induced S_{RN}1 mechanism



A typical example is shown in Figure 3, where the reduction of chloroquinoline is observed in the absence (dashed line) and in the presence of a nucleophile acetone enolate (full line). Wave D features the two-electron formation of ArH in the absence of nucleophile. When nucleophile is added, the decrease of the waves magnitude indicates that the substitution reaction occurs.

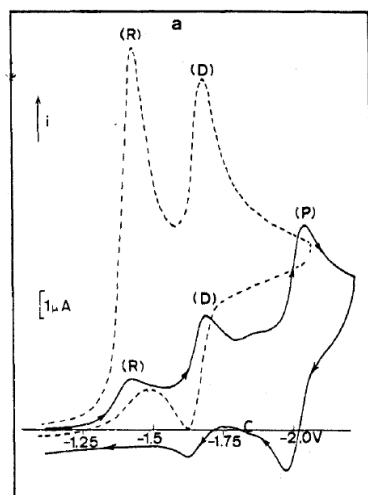


Figure 3. Cyclic voltammetry of 2-chloroquinoline (1.75 mM) in liquid NH₃ at -40°C. Scan rate 0.2 V/s. (dashed line) Without nucleophile added and (full line) in the presence of the nucleophile (0.025 M CH₂COCH₂⁻). Adapted from ref. 30.

Hence, analysis of current decrease as function of nucleophile addition allows for a quantitative analysis of the kinetics of

nucleophile addition on the intermediate radical. More specifically, as in the case of the ECE/DISP dichotomy, J-M. Savéant has provided a rigorous description, showing that the ECE/DISP/substitution competition is governed by two kinetic parameters involving both rate constants and operational parameters: $\sigma = k_C / k_{Nu} [\text{Nu}^-]$ and $\rho = (k_D C^0 / k_{Nu} [\text{Nu}^-]) ((Fv/RT)/k_C)^{1/2}$ (k_C is the rate constant of ArX•⁻ cleavage, k_{Nu} is the rate constant of nucleophile addition on Ar•, $[\text{Nu}^-]$ is the bulk concentration of

nucleophile, C^0 is the bulk concentration of the substrate ArX, k_D is the rate constant of homogeneous electron transfer, see Scheme 2). A 2D zone diagram was drawn (Figure 4) showing the domain of prevalence of each mechanism. This provides a unique tool to understand the paradox of such system in the sense that the electrochemical inducement (reduction of ArX producing ArX•⁻ and Ar• allowing the substitution to occur) involves the simultaneous destruction of the key species Ar• via its reduction (at the electrode or by ArX•⁻), which then stops the radical chain substitution process. In the ECE situation, reduction of Ar• at the electrode is prevented by its trapping by Nu⁻. Hence, σ has to be small for substitution to be dominant (bottom left of the zone diagram). In the DISP situation, $k_{Nu} [\text{Nu}^-]$ is opposed to k_D and has to be large again to favor substitution over homogeneous reduction. A large value of k_C is also favorable as it lowers the efficiency of the homogeneous reaction. However, k_C should not be too large otherwise the ECE mechanism is again dominant (e.g. progressive transition from SUBST to ECE-SUBST and then ECE zone as shown on the bottom part of Scheme 1).

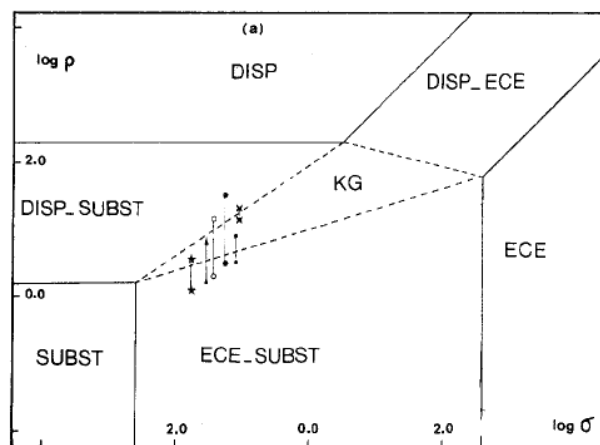


Figure 4. ECE-DISP-SUBST zone diagram. Adapted from ref. 30.

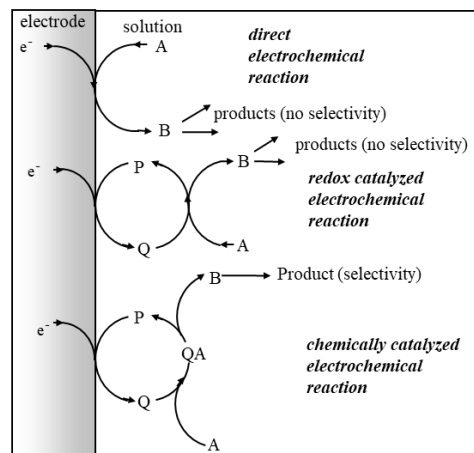
Deciphering the S_{RN}1 mechanism induced electrochemically was not only an achievement *per se* but it exemplifies how the tools of molecular electrochemistry can be used to study non-electrochemical reactions and get a deep understanding on how kinetic competition, including mass transport, can drive the efficiency or selectivity of chemical reactions.

The use of an electrode to perform an electrosynthesis at large scale requires the process to be studied under “real conditions”, *i.e.* corresponding to macroelectrolyses at large current densities with vigorous stirring of the solution or under flow conditions (circulation of the solution). The question on whether the information retrieved from analyses performed using analytical non-destructive methods such as CV can be transposed to predict product distribution in bulk electrolysis, for example, was of interest for J-M. Savéant as he always kept in mind that practical application is one of the final goals of studying reactions. Hence, together with C. Amatore they have provided a thorough description of **product distribution in preparative electrolysis**.^{33,34,35,36,37,38,39,40} They have shown that the establishment of the relationship between mechanism and governing parameters, on the one hand, and product distribution, on the other hand, requires similar approaches as those developed for CV. An interesting outcome is that the operational conditions, for example current density, can in some cases change the product distribution. This has been exemplified in the case of direct CO₂ reduction in DMF at a mercury electrode (oxalate vs. CO as products).⁴¹ This analysis could be profitable in the present context of revival of the synthetic organic electrochemistry.⁴²

Catalysis in Molecular and Biomolecular Electrochemistry

Molecular catalysis of electrochemical reactions is nowadays a very popular process. It is amazing to realize that molecular catalytic processes were of primarily interest of pioneers of molecular electrochemistry, with the first experimental illustration being reported almost six years after the formal derivation of the CV equations.^{43,44} The studied system was an inorganic system. Because in the following years the focus of molecular electrochemistry was on organic electrochemistry, catalytic processes were not explored until the concept of **redox catalysis** emerged. Redox catalysis corresponds to the reaction scheme shown on Scheme 3 (for the case of a reduction): the direct reduction of a substrate A is replaced by its reduction by the electrogenerated outersphere electron donor Q.^{45,46,47,48,49,50} As both the direct and indirect reduction of the substrate are outersphere, one may wonder why catalysis occurs. Why can the homogeneous reductant provide reduction of the substrate at more anodic potentials than the electrode? The answer is that the electrons are confined in a two-dimensional space at the electrode surface, whereas they are dispersed in a three-dimensional space once transferred on the redox catalyst.⁵¹ Therefore, redox catalysis can be named “physical catalysis”, the diffusion-reaction layer where reduction of the substrate occurs being viewed as a “volumic electrode” and the catalyst rather viewed as an electron mediator (Note that redox catalysis was developed around the same time by Henning Lund and coworkers⁵²).

Scheme 3. Redox catalysis vs. chemical catalysis



Redox catalysis proved to be a very useful tool to investigate short-lived intermediates such as anion radicals or cation radicals.^{53,54,55} Indeed, high scan rate CVs is source of kinetic information on the fate of electrogenerated species, but it is limited to the sub-microsecond domain (if ultramicroelectrodes are used) and so to the determination of first order rate constants as high as 10^7 s^{-1} at scan rate of $10^6 \text{ V}\cdot\text{s}^{-1}$. This is based on the rough estimation that the competing parameter $\lambda = k_C / (Fv / RT)$ (k_C being the rate constant of intermediate cleavage) should be less than 0.25 to get some reversibility. In the framework of redox catalysis, the short-lived species is obtained from an homogeneous electron transfer between the electrogenerated active form of the catalyst and the substrate. This uphill electron transfer is driven by the fast evolution of the short-lived intermediate. Provided the homogeneous electron transfer is at equilibrium, the catalytic response is governed by $\gamma = C^0 / C_{cat}^0$ (C^0 is the bulk concentration of the substrate A and C_{cat}^0 the bulk concentration of the catalyst P) and $\lambda_{cat} = k_C \exp\left(\frac{F}{RT}(E_{A/B}^0 - E_{P/Q}^0)\right) / (Fv / RT)$ where $E_{A/B}^0$ and $E_{P/Q}^0$ are the standard potential of the substrate and catalyst, respectively. As soon as $\lambda_{cat}\gamma$ is large enough (typically larger than 0.1), catalysis is observed in CV (*i.e.* $i_p / i_p^0 > 1$, where i_p is the CV plateau or peak current in the presence of substrate A, and i_p^0 the CV peak current of the catalyst alone) and k_C can be determined if both standard potentials are known. The upper limit for accessible k_C is dictated by the condition of the homogeneous electron transfer to remain at equilibrium, which implies typically that $k_{-e} C_{cat}^0 / k_C > 0.25$ (where $k_{-e} = k_{dif}$ is the backward homogeneous electron transfer rate constant, *i.e.* the rate constant for reaction between P and B, usually

assumed to be controlled by diffusion). In other words, whereas in the direct method the cleavage step rate constant is compared to the diffusion rate Fv/RT (controlled by the scan rate), in the indirect redox catalysis method k_C is compared to the downhill diffusion controlled backward homogeneous electron transfer, setting the upper limit to $k_C < 4k_{diff}C_{cat}^0 \approx 10^9 \text{ s}^{-1}$ taking $C_{cat}^0 \approx 0.05 \text{ M}$ as maximal accessible value.⁵⁶ Hence, the indirect method based on redox catalysis allows to determine intermediates lifetimes in the nanosecond regime. We note that getting faster and faster cleavage of bonds leads to the idea that the intermediate lifetime might be smaller than a vibration, hence leading to a concerted dissociative electron transfer. This idea (already proposed by N. S. Hush in 1952 and 1957⁵⁷) opened a new chapter of the fast field of electron transfer. We will review the important contribution of J.-M. Savéant in this field in the last section. In the case where the intermediate does exist, cleavage of aromatic halides (ArX) was studied and rate constants have been gathered by several research groups from both direct and indirect electrochemical measurements, as well as from pulse radiolysis over many orders of magnitude. Interestingly the logarithm of these rate constants shows a rough linear correlation with the standard rate constant for the formation of the anion radical (Figure 5). These data were rationalized within the framework of the model of intramolecular dissociative electron transfer (see last section) including an out-of-plane bending of the cleaving bond allowing avoidance of a conical intersection.⁵⁸ It is a salient example where the use of a methodology developed for molecular electrochemistry allows to decipher and to illustrate important and general Physical Chemistry phenomena.

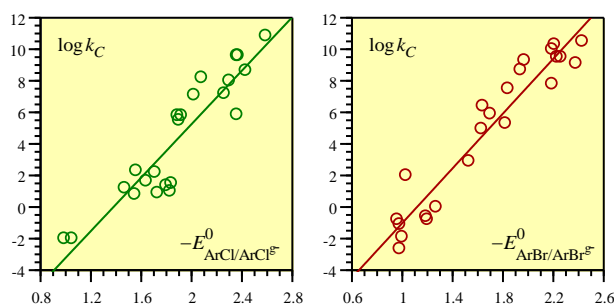


Figure 5. (left) Correlation between the cleavage rate constants and the standard potential for aryl chlorides. From left to right: Ar[•]: 2-nitrophenyl, 4-nitrophenyl, 9,10-chloroanthracenyl, 4,4'-chlorobenzophenone, 2-benzaldehyde, 4-benzoylphenyl, 9-anthacenyl, 1-anthacenyl, 2-anthacenyl, 3-acetylphenyl, 4-(2-(4-pyridyl)-vinyl)phenyl, 4-quinolyl, 4-acetylphenyl, 2-quinolyl, ethyl 4-benzoate, 4-cyanophenyl, 1-naphthyl, 2-naphthyl, 3-pyridine, 2-biphenyl, 2-pyridine, 3-biphenyl, 4-biphenyl. (right) Correlation between the cleavage rate constants and the standard potential for aryl bromides. From left to right: Ar[•]: 2-isopropyl-4-nitrophenyl, 4-nitrophenyl, 2-methyl-3-nitrophenyl, 2-methyl-4-nitrophenyl, 2-nitrophenyl, 3-fluorenyl, 1-fluorenyl, 2,6-dimethyl-4-nitrophenyl, 3-benzoylphenyl, 4-benzoylphenyl, 5-methoxy-psoralenyl, 9-

anthacenyl, 3-acetylphenyl, 4-acetylphenyl, 4-benzonitrile, ethyl-4-benzoate, 1-naphthyl, 1-naphthyl, 2-naphthyl, 3-pyridine, 2-pyridine, 3-biphenyl, 4-biphenyl. Adapted from ref. 58.

Reduction of organic halides does not necessarily occur *via* an outersphere electron transfer. If there is a more intimate contact between the electrogenerated reductant and substrate, then we enter the realm of **chemical catalysis** (Scheme 3). Chemical catalysis is superior to redox catalysis as it allows for not only avoid high energy intermediates, but also for controlling reaction selectivity. It has been illustrated by J.-M. Savéant⁵¹ *via*, for example, a thorough study of the reduction of vicinal dibromides with electrogenerated aromatic anion radicals (redox catalysis) or transition metals porphyrins (chemical catalysis).⁵⁹ The plot of the catalytic rate constants measured by cyclic voltammetry as a function of the driving force of the homogeneous reduction reaction shows (Figure 6) that the Zn and Cu porphyrins behave as outer-sphere electron donors, as does the free base, whereas the Co, Fe and Ni data points stand well above the outer-sphere line. This example is the occasion to highlight the important role of the late Doris Lexa, a longtime collaborator of J.-M. Savéant in the domain of bioinspired molecular electrochemistry and in particular on the electrochemistry of vitamin B12⁶⁰ and iron porphyrins and their catalytic activity.

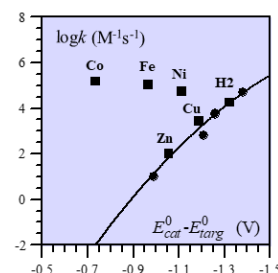
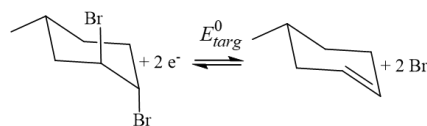


Figure 6. Catalysis of the electrochemical reduction of 1,2-dibromocyclohexane into the corresponding olefin (Scheme 3) in DMF + 0.1 M Bu₄NBF₄ by anion radicals of aromatic hydrocarbons (solid circles) and by the redox couples obtained by one-electron reversible reduction of ETIOP porphyrins (see Figure 2 for the definition of the ETIOP ring) of Co^{II}, Fe^{II}, Ni^{II}, Zn^{II}, Cu^{II} and the free base (H2) (solid squares), from the data in ref. 59. The full line represents the fitting of these data points by the quadratic law for the dissociative electron transfer by outer-sphere one-electron donors according to the Morse curve model.¹¹¹

As shown above, the concept of homogeneous catalysis of electrochemical reactions has gained popularity for redox organic transformations in the late 80's,⁶¹ but J.-M. Savéant also saw its potentiality for the activation of small molecules, in particular CO₂ reduction.^{62,63} It is worth mentioning that he was involved in the field of CO₂

electroreduction for a long time with several important contributions to the direct reduction of CO₂,^{64,41} in particular the determination of the standard potential of the CO₂/CO₂⁻ couple in aprotic dimethylformamide (-2.2 V vs. SCE).⁶⁵ Molecular catalysis of electrochemical reactions is now experiencing its golden age *via* the thriving development of small molecules activation with transition metal complexes as molecular catalysts. In front of this contented situation, it was necessary to get a rational benchmarking of catalysts for a given reaction. Although the concept of diffusion-reaction layer for catalysis in pure kinetics conditions was known for a long time, it was the occasion to highlight its importance for an adequate evaluation of the turnover frequency (*TOF*) of a catalyst and its relationship with the applied potential in the case of the simple mechanism depicted in Figure 7.⁶⁶ This led to the introduction of the catalytic Tafel plots relating *TOF* to overpotential (defined as the difference between the electrode potential and the standard potential of the targeted reaction).

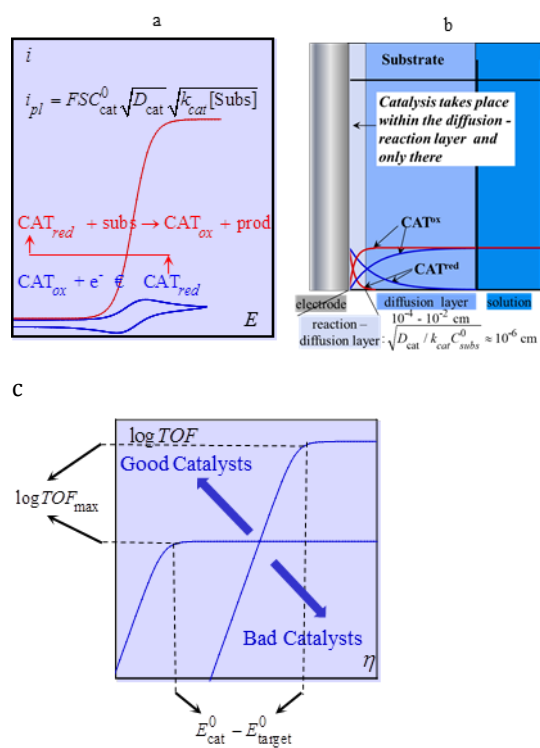


Figure 7. One-electron/one step catalytic reaction scheme under canonical conditions. (a) Reaction scheme and its current-potential response in the absence (blue) and presence (red) of the substrate, as well as equations of the plateau current. (b) Concentration profiles in the absence of substrate (blue) and in canonical conditions (red). The representation takes the case of a reductive process as example. Transposition to oxidations is straightforward with the help of appropriate changes of sign. *i*: current, *E*: electrode potential. E_{cat}^0 : standard potential of the CAT_{ox}/CAT_{red} redox couple. i_{pl} : plateau current. *S*: electrode surface area. C_{cat}^0 : bulk concentration of the catalyst. D_{cat} : average of the diffusion coefficients of all forms of catalyst. k_{cat} : second order rate constant of the catalytic step. [Subs]: concentration of sub-

strate. (c) Catalytic Tafel plot.

Extraction of the catalytic rate constant is easily performed from the plateau current obtained in canonical conditions for mechanisms where the rate determining step is the first irreversible chemical step following the catalyst activation. Note that if the plateau current is not reached, increasing the scan rate or analysis of the foot-of-the wave may be an alternative strategy.⁶⁶ This methodology was used intensively to explore CO₂ reduction with catalysts from the family of iron porphyrins. J.-M. Savéant's group first emphasized the crucial role of acids in bolstering the catalytic rate.⁶⁷ Then, taking advantage of the knowledge gathered on proton-coupled electron transfer and its coupling with bond breaking processes, the mechanism was studied in details leading to a rational design of a more efficient catalyst.⁶⁸ Similarly, analysis of substituents effects revealed an "iron" law correlating the standard potential of the catalyst and the catalytic rate constant, again illustrating that molecular electrochemistry is a convenient tool to decipher physical chemistry laws of reactivity.⁶⁹ It was however shown that the "iron law" can be broken by introducing through space electrostatic effects leading to a highly efficient molecular catalyst for the conversion of CO₂ to CO (Figure 8).⁷⁰

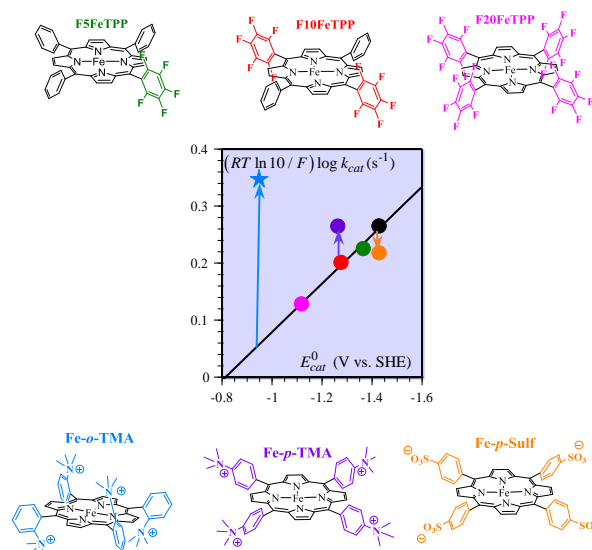


Figure 8. Molecular catalysis of CO₂ to CO reduction with iron porphyrins. Catalytic rate constant as function of the standard potential of the Fe(0)/Fe(I) couple. Adapted from ref. 70.

An important lesson that collaborators of J.-M. Savéant learned by working at his side is that basic laws of Physical Chemistry cannot be escaped and that pitfalls in reasoning or data analysis should be tracked to avoid misadventures. We already mentioned instrumentation artifacts that he revealed.²⁸ In the field of catalysis of electrochemical reactions, many traps can be met and he considered as an important task to make sure that false ideas or reasoning do not propagate.⁷¹ One of the last misanalysis he fought against was the idea that the maximal turnover frequency of a homogeneous catalysis of an electrochemical reaction could be correlated to the equilibrium free energy of the reaction.⁷² Such an intermingling of rate constants, standard quantities and concentration is misleading as was the

flawed concept of pH dependent driving force for proton-coupled electron transfer.⁷³

Because J.-M. Savéant was very cautious on experimental results, as already mentioned, he got involved in the design of potentiostats able to adequately correct CVs for ohmic drop. Correction for ohmic drop is also important for catalytic CVs (except for the plateau current) if one aims at retrieving kinetic information from the shape of the wave, in particular the effect of electron transfer between the electrode and the catalyst.^{44,74} In that regard another pitfall is that the surface state of the electrode might be source of errors. In molecular electrochemistry, it is generally preferred that the electrode behaves as an outersphere electron donor or acceptor. Even considering this state of affair, artifacts are still possible as partial coverage of the electrode surface by an isolating film can lead to an apparent slowness of the electron transfer. This has been demonstrated by J.-M. Savéant and C. Amatore in a seminal paper,⁷⁵ showing the effect of constrained diffusion around active sites. This constrained diffusion may actually also occur at the entrance of a thick coating with channels and containing **immobilized molecular catalysts**. Then, the next step is the question of transport of both substrate and electron through this catalytic film and their entanglement with the catalytic reaction. The contribution of J.-M. Savéant in this field is also very important and started in 1978 when the interest of redox polymers and modified electrode for catalysis was growing.⁷⁶ An analysis of electron transport by hopping in such films was provided leading to a modified Nernst-Planck equation,⁷⁷ the description being later refined by consideration of percolation effects.⁷⁸ Ohmic conduction in mesoporous electrodes was also more recently studied considering a transmission line model as initially introduced by R. De Levie,⁷⁹ the effect of ohmic drop being carefully analyzed.⁸⁰ Note that this question is intimately related to the field of electrochemical energy storage, a domain of recent interest for J.-M. Savéant to which he contributed *via* the revisit of the notion of "pseudocapacitance" initially proposed by B. Conway.⁸¹

Kinetics of electrochemical reactions mediated by derivatized electrodes or redox polymers films with electron hopping as electron transport was thoroughly investigated in the framework of steady-state methods (rotating disk electrode)^{82,83,84,85,86,87,88} and more recently in the framework of cyclic voltammetry.^{89,90,91} Considering fast catalysis, the interplay of electron transport, substrate transport and catalytic reaction is conveniently represented *via* the kinetic zone diagram shown in Figure 9 for a simple one step mechanism. Application of the formal description to several experimental systems was achieved through a fruitful collaboration between J.-M. Savéant and the group of F. Anson at Caltech.^{92,93} This collaboration led to further developments in which the role of charge transport relay and catalysts are separated *via* the incorporation of a redox shuttling species within the film. This was illustrated with the catalytic oxygen reduction by a cobalt porphyrin as catalyst (Scheme 4).⁹⁴ Another refinement of the modelling was done in collaboration with the group of A. J. Bard at the University of Texas with the introduction of a finite mass transfer rate of the substrate

across the film-solution interface.⁹⁵ Studies of molecular catalysts immobilized in a film coated on the surface of an electrode are currently experiencing a lot of interest in the context of contemporary energy challenges and in particular for CO₂ reduction.⁹⁶

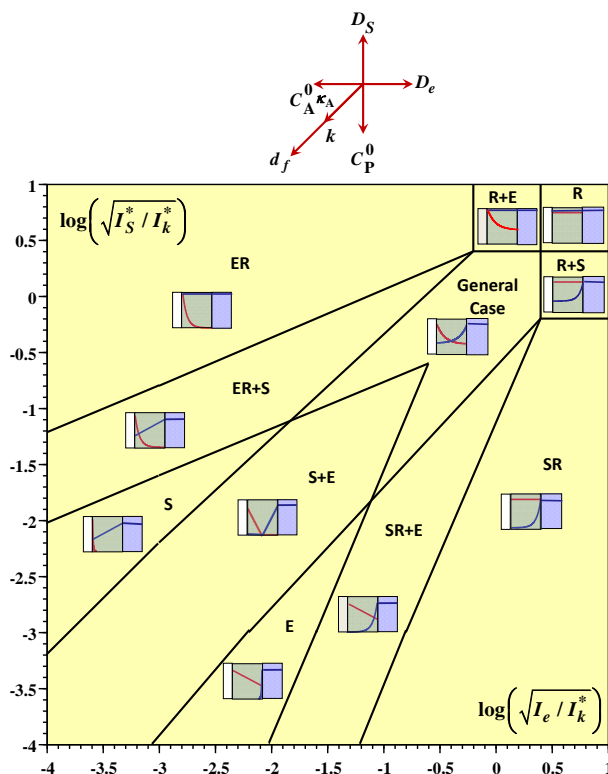
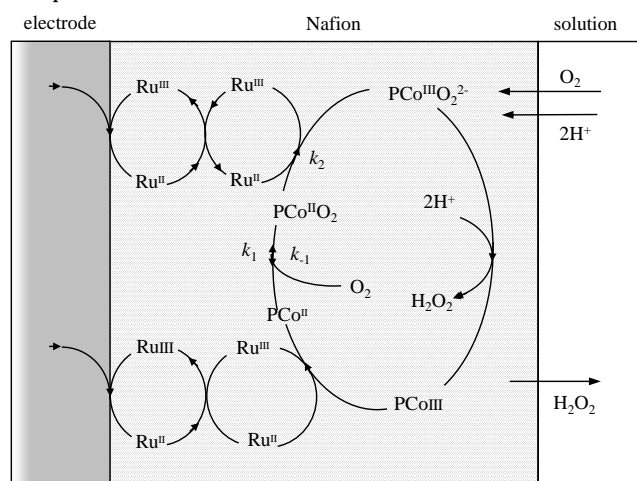


Figure 9. Kinetic zone diagram. The arrows above the diagram allows traveling through the zone diagram upon varying the experimental parameters, in direction and magnitude (log). The inserts show the concentration profiles of the reduced catalyst (red) and substrate (blue). Adapted from ref. 91.

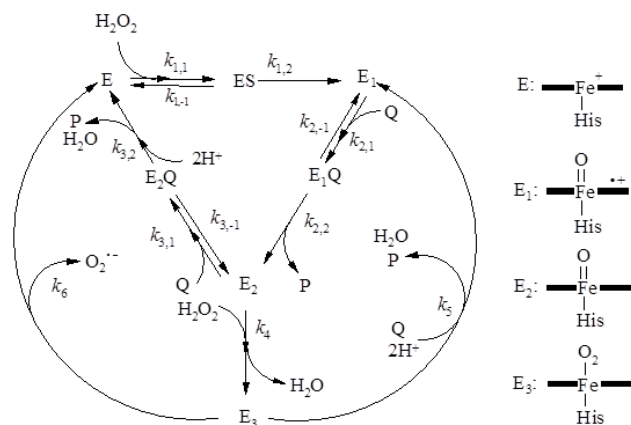
Scheme 4. Catalysis of the reaction of O₂ by Ru(NH₃)₆²⁺ - Co(II)tetrakis(4-*N*-methylpyridyl)porphyrin-Nafion film. Adapted from ref. 94.



From the early days of molecular electrochemistry, J.-M. Savéant was well aware that the concepts developed, in

particular for catalysis, were useful not only in the field of organic electrochemistry, which was developing fast at that time, but also in the field of coordination chemistry as shown by its intensive work on vitamin B12.⁶⁰ Beyond molecular electrochemistry the concepts are also useful to develop the field of biomolecular electrochemistry. It is the reason that he got increasingly involved in problems of biological interest. This was particularly true when Jacques Moiroux⁹⁷ joined the Laboratoire d'Electrochimie Moléculaire in 1989 together with his close collaborator Agnès Anne. Their work was first to focus on the study of NADH analog electrochemistry.⁹⁸ Starting in 1993, they got involved in a systematic electrochemical approach to **enzymatic catalysis** using redox mediators to shuttle electrons between the electrode and the prosthetic group of an enzyme. Catalytic processes were modeled using "Ping-Pong" mechanisms for both enzymes in solution^{99,100,101,102}, or immobilized at the electrode surface in the form of monolayers^{103,104,105} or organized multilayers.^{106,107} A typical application is the well-studied glucose oxidase which mechanism has been deciphered in details using one-electron redox mediators¹⁰⁰ thanks to the important work of Christophe Demaille who is now leading the group "Biomacromolecular Systems – Electron Transport at the Nanoscale" at the Laboratoire d'Electrochimie Moléculaire. Interestingly, it was shown that a precursor complex is formed between the mediator and a site close to the Flavin prosthetic group. This precursor complex allows for molecular differentiation of the enzyme between non-natural redox mediators.¹⁰⁰ Another piece of work was the thorough analysis of the Horseradish Peroxidase (HRP) mechanism (Scheme 5).

Scheme 5. Mechanism of the Horseradish Peroxidase (HRP)



HRP has attracted a lot of attention as it is involved in a number of biotechnological applications, but its catalytic process is complex as revealed by the crossings of the catalytic currents observed in cyclic voltammetry in the presence of a redox mediator and increasing concentrations of the substrate H_2O_2 . The behavior was fully explained *via* the mechanism depicted in Scheme 5, which involves the intricate coupling between the inactivation of the enzyme by the substrate itself (through the formation of compound E_3) and its reactivation by both the spontaneous release of superoxide (step k_6) and the reduction of

the inactivated enzyme by the reduced form of the mediator (k_5).¹⁰¹ A new function "lms", named after Limoges-Moiroux-Savéant, had to be introduced to describe the CVs involving superposition of catalysis with activation and inhibition. Using all experimental observations, a thorough characterization of the mechanism was possible leading to a simulation of the CVs in all conditions including unusual hysteresis and trace crossing features.¹⁰¹

As seen above, the work of J-M. Savéant in the field of catalysis encompassed many aspects and always associated formal and conceptual development to experimental illustrations.

Dissociative Electron Transfer – Proton Coupled Electron Transfer

As already indicated, the study of bond cleavage in transient ion radicals or radicals formed by electron transfer led to the idea that the intermediate lifetime might be smaller than a vibration, hence corresponding to a **concerted dissociative electron transfer**. Evidences were first gathered from low-temperature γ irradiation coupled by ESR characterization for aliphatic halides reductive cleavage.¹⁰⁸ In 1985 and 1986, J-M Savéant and coworkers reported that the kinetics of homogeneous and heterogeneous reduction of aliphatic halides is consistent with a concerted dissociative electron transfer driven by the standard potential of $\text{RX/R}^+ + \text{X}^-$ couple.^{109,110} Importantly, a non-linear activation-driving force relationship was revealed which could be approximated by a quadratic Marcus-Hush type equation. However, the outersphere electron transfer model developed by Hush and Marcus does not apply to concerted processes as the harmonic vibration approximation for the internal reorganization energy is not compatible with the cleavage of a bond. This prompted for the development of an adequate model proposed in 1987.¹¹¹ A two states model was considered with a Morse curve approximation of the energy of the cleaving bond in the reactant and on the assumption that the repulsive interaction of the fragments product is the same as the repulsive part of the reactant Morse curve (Figure 10). This leads to a quadratic activation-driving force relationship with a contribution to the reorganization energy being D_b , the bond dissociation energy of the cleaving bond.

$$\Delta G^\ddagger = \Delta G_0^\ddagger \left(1 + \frac{\Delta G^0}{4\Delta G_0^\ddagger} \right)^2 \quad \text{with} \quad \Delta G_0^\ddagger = \frac{D_b + \lambda_0}{4}$$

ΔG^\ddagger is the free enthalpy of activation, ΔG^0 is the standard free enthalpy of the reaction, and λ_0 is the solvent reorganization energy.

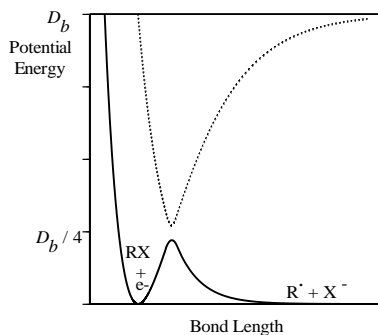


Figure 10. Morse curve model for a concerted dissociative electron transfer.

Application of the model to the homogeneous dissociative electron transfer on alkyl halides¹¹¹ as well as reduction of organic peroxides gives quantitative agreement.¹¹² Cyclic voltammetry appears as a very useful tool to identify concerted dissociative electron transfers. Approximating the rate law for a concerted dissociative electron transfer by the classical Butler-Volmer law leads to a transfer coefficient

$$\alpha = \frac{\partial \Delta G^\ddagger}{\partial \Delta G^0} = \frac{1}{2} \left(1 + \frac{\Delta G^0}{D_b + \lambda_0} \right) = \sqrt{\frac{\Delta G^\ddagger}{D_b + \lambda_0}}$$

This transfer coefficient is significantly smaller than 0.5, the typical value for an outersphere electron transfer. Indeed, in cyclic voltammetry, at a given scan rate, the activation free energy at the peak, ΔG_p^\ddagger , is given by

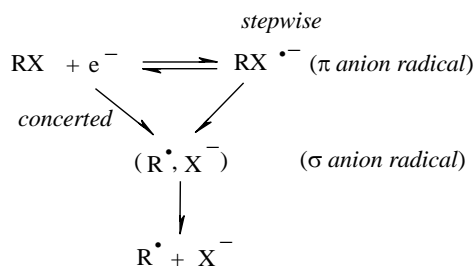
$$\Delta G_p^\ddagger = \frac{RT}{F} \left[\ln \left(k_S \sqrt{\frac{RT}{\alpha F v D}} \right) - 0.78 \right]$$

indicating that its value is roughly similar for both a dissociative and an outersphere electron transfer (D is the diffusion coefficient of the substrate, v is the scan rate and k_S is the standard rate constant for electron transfer). Therefore, because the reorganization energy is much larger for the dissociative process ($D_b \gg \lambda_i$, λ_i being the internal reorganization energy for outersphere electron transfer), it can be concluded that $\alpha_{\text{dissociative}} \ll \alpha_{\text{outersphere}} \approx 0.5$. As the peak width in CV

given by $E_{p/2} - E_p = 1.857 \frac{RT}{\alpha F}$ (E_p is the peak potential and $E_{p/2}$ is the potential at the half-wave), it is concluded that the broadness of a wave is a strong criterion for a concerted pathway. This has been illustrated by many examples and it was shown that the molecular structure can control the occurrence of a stepwise or a concerted mechanism (Scheme 6). Among the key factors are the standard potential of the anion radical (low lying π^* orbital or not), weak or strong bond dissociation energy, oxidability of the leaving group.^{113,114,115} It is worth noting that aryl diazonium cations appear as good candidate for a concerted mechanism. However, their reduction at a glassy carbon electrode leads to derivatization of the electrode *via* grafting of the generated neutral radical as discovered by Jean Pinson, a longtime collaborator of J.-M. Savéant.¹¹⁶ Several refinement and extension of the model were pro-

posed. One concerns the possible interaction of the dissociated fragments in the solvent cage (σ anion radical) and its effect on the cleavage dynamics.¹¹⁷ Other concerns the description of the cleavage step of the π anion radical as an intramolecular concerted dissociative electron transfer (see Figure 5 and the corresponding text).⁵⁸

Scheme 6. Dissociative electron transfer



e^- : electrode, homogeneous donor
(ground state, excited state)

So far, the existence of a concerted mechanism has been intuited from the consideration that the primary radical intermediate following electron transfer lives less than a vibration. In other words, it does not exist. However, an important result from J.-M. Savéant work was to show that a transition between stepwise and concerted mechanisms can occur upon changing the driving force as sketched on Figure 11. Again, cyclic voltammetry is a convenient tool to trigger and exemplify this phenomenon as it allows for an easy measurement of the rate of the electrochemical reaction as function of its driving force, which is varied as the electrode potential is scanned. The rate constant can be extracted at any potential using the convolution technique (see first section). Alternatively the rate constant can be measured at the peak potential at various scan rates because, as surprising as it may seem at first sight, increasing the scan rate amounts to change the driving force at the peak potential. Consequently, raising the scan rate in cyclic voltammetry may trigger a transition from a concerted to a stepwise mechanism.¹¹⁹

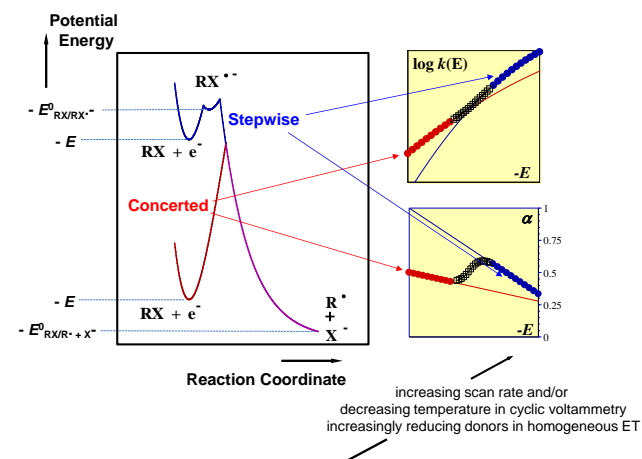


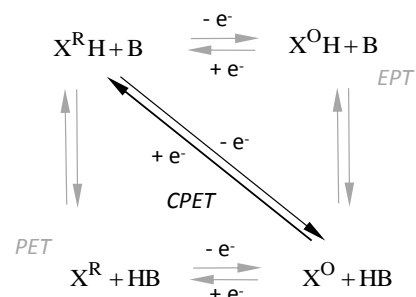
Figure 11. Potential energy profiles for the concerted and stepwise mechanism and variation of the rate constant and the transfer coefficient when passing from the concerted to the stepwise mechanism. Adapted from ref. 118.

As shown on Figure 11, because outersphere electron transfer and concerted dissociative electron transfers have similar quadratic activation-driving force relationship, but different reorganization energies and different apex, their rate constant vs. potential curvature are different and the transition between stepwise and concerted mechanism can be diagnosed from the evolution of the transfer coefficient α as function of potential. Then transition is characterized by an “ α wave” which was exemplified experimentally on several systems,^{119,120} not only from J-M. Savéant’s group.¹²¹ Transition from concerted to stepwise mechanism upon changing the driving force was also shown in the case of homogeneous reduction of 4-nitrobenzyl and 4-nitrocumyl chlorides.¹²² The very slow rate constant at small driving force was measured thanks to the amplification provided by an S_{RN1} chain process. This was in turn the occasion to explain how thermal S_{RN1} reactions discovered by N. Kornblum in 1975 work, thus illustrating the possible role of concerted vs. stepwise dissociative electron transfer in organic chemistry.¹²² Remarkably, the concept of concerted dissociative electron transfer has been used in photo-induced electron transfer chemistry and was initially thought as an attractive manner of fighting back-electron transfer to the ground state for systems in which the donor and/or the acceptor in the ion-pair undergoes fragmentation. Intuitively, it seems as an ideal situation that would lead to a unity quantum yield. And thus, a quantum yield below 1 would be the signature of a sequential two-step mechanism. J-M. Savéant and collaborator have shown that a purely dissociative photo-induced electron transfer is in fact not necessarily endowed with a unity quantum yield.¹²³ This is related to the fact that the system could partition between and back-electron transfer and cleavage in the funnel offered by the upper first-order potential energy surface combining the ground state and fragments zero-order surfaces. It was an additional illustration of irrigation of a physical chemistry field from concept issued from electron transfer reactivity studied by electrochemistry.

The above description and models apply to the cleavage of bonds between heavy atoms. However, processes involving the cleavage of a bond with an hydrogen, *i.e.* proton transfer, H-atom transfer (HAT) or **proton-coupled electron transfer (PCET)** are of utmost importance in chemistry and biology. The question of the competition between electron transfer + proton transfer vs. HAT was investigated by J-M. Savéant as it is in the core of many processes in organic electrochemistry.¹²⁴ J-M. Savéant was also very interested in investigating C-H bond cleavage in particular cation radical deprotonation in collaboration with J. Moiroux.^{125,126} After a first attempt to model such proton transfer reactions,¹²⁷ influenced by the important work of J.T. Hynes,¹²⁸ he took into account that the proton cannot be described classically and then included in the analysis the quantum character of the proton, enabling to reconsider the concept of imbalance of proton transfer.¹²⁹ It is worth noting that this concept, also named principle of imperfect synchronization, was recently reactivated at the occasion of a remarkably study of C-H oxidation of substituted fluorenyl-benzoates.¹³⁰ J-M Savéant showed in his very last published paper that the data can be rather ra-

tionalized *via* a transition between concerted and stepwise mechanisms upon changing the driving force as developed in the dissociative electron transfer context.¹³¹ Investigation of the intimate pathways for PCET involving different sites for proton transfer and electron transfer, which is the typical case for an electrochemical PCET, indeed bears some similarities with dissociative electron transfer as it required to identify criteria able to discriminate between stepwise and concerted processes (Scheme 7).

Scheme 7. Proton Coupled Electron Transfer, concerted (black) and sequential (grey) pathways.



However, in most cases, differences are at least twofold: (i) proton transfer are often fast and at equilibrium, (ii) the kinetic model describing the concerted pathway cannot be akin to the Morse curve model due to the quantum character of the transferring proton. Thus, J-M. Savéant and coworkers proposed a kinetic model for electrochemical concerted proton coupled electron transfer (CPET) based on a double Born-Oppenheimer type approximation which treats the electron as a fast sub-system with respect to the proton and the proton as a fast sub-system with respect to heavy-atoms displacements (Figure 12).¹³²

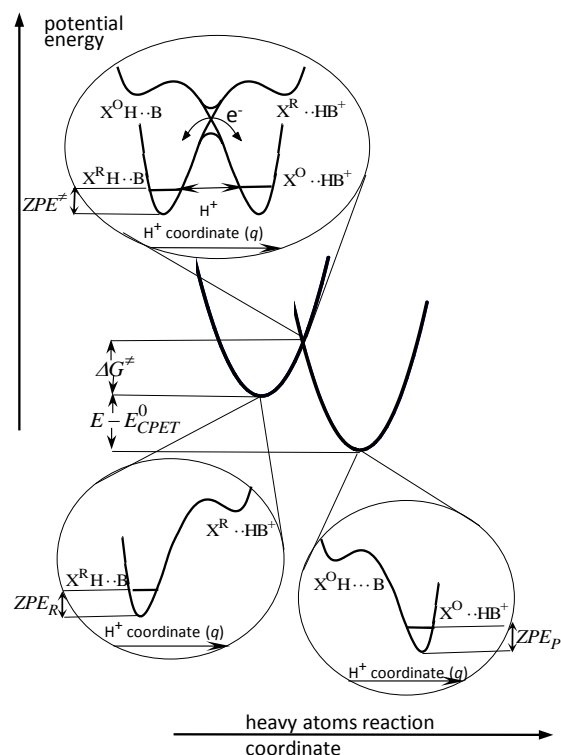


Figure 12. CPET mechanism. Both reactants and product electronic state potential energies as a function of heavy-atoms reaction coordinate are described by parabolas. Inserts show potential energies as a function of proton coordinate. Adapted from ref. 132.

Several experimental examples identifying CPET pathways have been reported both in organic solvent¹³³ and in water.¹³⁴ In the later, it is important to mention that the role of water as proton acceptor has been scrutinized in details, combining electrochemical¹³⁵ and photoinduced¹³⁶ approaches, and that the notion of pH-dependent driving force was showed to be incorrect.⁷³

A further step was achieved when it was shown experimentally that both CPET and dissociative electron transfer can combined in a single step making the cleavage of a bond upon reduction beneficial of the whole driving force of the reaction thanks to an appending acid-base function (Figure 13).¹³⁷ The role of appending acid-base functionalities as proton relays has been widely developed in the context of molecular catalysis and J-M. Savéant, in his never-ending quest for rational analysis, recently provided a kinetic description of the origin and limitations of boosting effects.¹³⁸

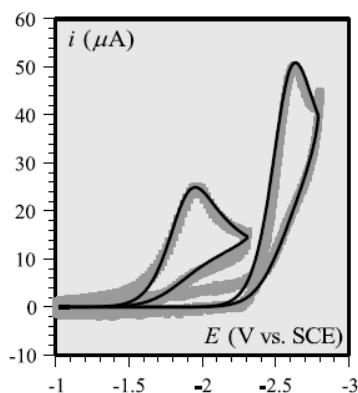
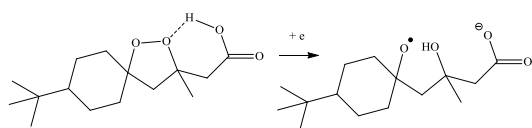


Figure 13. Thick gray lines: cyclic voltammetry of 2 mM the compound shown above (left) and the corresponding ester (right) in DMF at 0.2 V/s, at a glassy carbon disk electrode. Black thin lines: simulations. Adapted from ref. 137.

Finally as an emblematic example, we would like to mention the demonstration that an all concerted heavy atoms bond intramolecular dissociative CPET is at play in the catalytic process of CO₂ to CO conversion with iron porphyrins in the presence of Brønsted acids.¹³⁹ This would not have been possible without the patient establishment and illustration of various concepts by J-M. Savéant and coworkers over decades. This example shows how the concepts assemble to each other to enlighten complex systems.

Conclusion

Prof. Jean-Michel Savéant was a giant of electrochemistry.

With an over sixty years career, his legacy in the field is huge and he can be considered as one of the fathers of molecular electrochemistry. Besides, we think that the various, but not exhaustive, examples shown in this review illustrate how J-M. Savéant work irrigates many fields of physical chemistry such as photochemistry and material sciences, biochemistry, radical chemistry and synthetic chemistry including electron transfers, as well as all facets of catalysis where molecules play a role. The extreme rigor of the studies combined to the formal description of the electrochemical systems under investigation are the real two pillars of the apparent simplicity and elegance of J-M. Savéant work. Along with well-chosen illustrative experimental examples it has allowed to feed the establishment of structure-reactivity relationships and a thorough understanding of intimate reactivity at the molecular scale. It will remain a strong source of inspiration for all scientists interest by electron transfer chemistry.

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