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# Breaking Bonds with Electrons and Protons. Models and Examples

CYRILLE COSTENTIN, MARC ROBERT, JEAN-MICHEL SAVÉANT,*
AND CÉDRIC TARD

Université Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, Unité Mixte de Recherche Université - CNRS N° 7591, Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France

CONSPECTUS

Besides its theoretical interest, the attention currently aroused by proton-coupled electron transfers (PCET reactions) has two main motives. One is a better understanding of biological processes in which PCET reactions are involved, Photosystem II as well as a myriad of other natural systems. The other is directed toward synthetic processes, many of which are related to global

$$Y^O-X + H-A \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Y^R + X-H + A^-$$

all in concert ?

energy challenges. Until recently, the analyses of the mechanism and reactivity of PCET reactions have focused on outersphere transfers, those in which no bond between heavy atoms (all atoms with the exception of H) is concomitantly formed or broken. Conversely, reactions in which electron transfer triggers the breaking of a heavy-atom bond with no proton transfer have been extensively analyzed, both theoretically and experimentally. In both cases, strategies have been developed to distinguish between stepwise and concerted pathways. In each case, kinetic models have been devised, allowing the relation between activation and thermodynamic driving force to be established by means of parameters pertaining to the initial and final state. Although many natural and artificial processes include electron transfer, proton transfer, and heavy-atom bond breaking (/formation), no means were offered until recently to analyze the mechanism of such reactions, notably to establish the degree of concertedness of the three constitutive events. Likewise, no kinetic models were available to describe reactions where the three events are concerted. In this Account, we discuss the strategies to distinguish stepwise, partially concerted (when two of the three events are concerted), and totally concerted pathways in these reactions that include electron transfer, proton transfer, and heavy-atom bond breaking. These mechanism analysis methods are illustrated and validated by three examples. First we describe the electrochemical cleavage of an O−O bond in an aliphatic peroxide molecule with a pendant carboxylic acid group that can serve as proton donor for electron transfer and bond breaking. In the second example, we examine the breaking of one of the C−O bonds of CO_2 within a multistep process where the reduction of CO_2 into CO is catalyzed by an electrogenerated iron(0) porphyrin in the presence of various Brönsted acids. In this case, an intramolecular electron transfer triggers proton transfer and bond cleavage. In the first two examples, all three events are concerted. The third example also involves catalysis. It describes the cleavage of a cobalt−carbon bond in the reduction of chloroacetonitrile catalyzed by an electrogenerated cobalt(I) porphyrin. It illustrates the rather common case where the intermediate formed by the reaction of a transition metal complex with the substrate has to be cleaved to close the catalytic cycle. In the first two examples, all three events are concerted, whereas, in the last case, a partially concerted pathway takes place: proton transfer and bond-breaking (Co−C cleavage) are concerted after an initial electron transfer step. The all-concerted cases require a model that connects the kinetics to the thermodynamic driving force of the reaction. Starting from previous models of outersphere electron transfer, concerted proton-electron transfer, and concerted dissociative electron transfer, we describe a model for all-concerted proton−electron-bond breaking reactions. These pathways skip the high-energy intermediates that occur in stepwise pathways, but could introduce kinetic penalties. The all-concerted model allows one to assess these penalties and the way in which they can be fought by the supplement of driving force offered by concerted proton transfer.
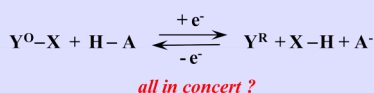
1. Introduction

An essential breakthrough in the predictive modeling of chemical reactivity was achieved when semiclassical models of single electron transfer appeared. The MHL (Marcus−Hush−Levich[1−3]) model of outersphere[4−6] electron transfer in its electrochemical version and its homogeneous kinetics version thus allowed replacing empirical rate vs driving force correlations by predictive relationships derived from the properties of the initial and final states. The parameters derived from application of the empirical correlations to the

experimental data (transfer coefficient and standard rate constant in electrochemistry, symmetry factor and self-exchange rate constant in the homogeneous electron transfer kinetics) could then be given a precise physicochemical meaning thanks to the predicted activation free energy/driving force relationship and the degree of adiabaticity of the reaction.[7]

Electrochemical reactions or homogeneous redox reactions are seldom simple outersphere electron transfers. Availability of the above models is however precious in the numerous cases where outersphere electron transfers are the rate-determining steps of multistep reaction sequences. A typical example is provided by the coupling between electron and proton transfers where the latter may be so fast as to remain unconditionally at equilibrium.[8]

One drawback of the MHL model is that it is restrained to outersphere electron transfers, that is, to reactions during which bond cleavage or formation are not concerted with electron transfer. The next step was thus the elaboration of a model of "concerted dissociative electron transfer," that is, a reaction in which electron transfer is concerted with the cleavage of a bond between two heavy atoms. The model was based on a Morse curve potential energy profile for the bond to be cleaved and a repulsive Morse curve for the broken bond.[9,10] It has been validated by numerous experimental examples involving electrochemical electron transfers as well as thermal or photochemical homogeneous electron transfers.[10]

Moreover, the coupling between electron transfer and proton transfer is ubiquitous in natural and artificial processes as witnessed at the thermodynamic level by the considerable number of available Pourbaix diagrams relating equilibrium potentials and pH. Besides its own fundamental interest, the analysis of these proton coupled electron transfer (PCET) reactions has two main motivations. One is the comprehension of biological systems in which PCET reactions are involved, for example, but not exclusively Photosystem II.[11,12] The other is related to modern energy challenges requiring the activation of small molecules as in the splitting of water into hydrogen and oxygen,[13,14] the reduction of oxygen,[15,16] and the reduction of CO_2.[17,18] Until recently, mechanism analysis and models have been restricted to the cases where proton transfer is associated with an outersphere electron transfer. The reaction may follow stepwise pathways, PET (proton transfer first followed by electron transfer) or EPT (electron transfer first followed by proton transfer), as sketched in Scheme 1. It may also follow a concerted pathway (CPET, green oblique line in

SCHEME 1[a]
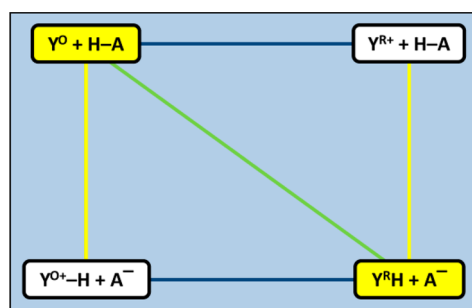
[a]Blue, electron transfer; yellow, proton transfer; green, concerted proton–electron transfer.

Scheme 1).[19] Distinction between stepwise and concerted pathways has been an important objective in the investigation of PCET reactions.[20–22] The MHL model of outersphere electron may be applied to the electron transfer steps in the stepwise pathways. Specific models have been devised for the CPET case,[23,24] based on the ideas previously developed for proton transfer,[25] and successfully applied to the oxidation of phenols.[26,27]

In the above-mentioned activation of small molecules, the reduction of dioxygen into water and the reduction of CO_2 into CO or further reduced products imply not only the coupling of proton and electron transfers but also the coupling of these two events with the breaking of a bond linking two heavy atoms (heavy as compared to electrons *and* protons). Understanding, in terms of mechanism and reactivity, the way in which these three events are associated is a fundamental question that goes beyond these two examples of current interest.

Scheme 2 provides a three-dimensional depiction of the various intermediates that should be considered and the various pathways that may be followed to go, oxidatively or reductively, from reactants to products. It shows the completely stepwise pathways where the three events occur successively and also the partially concerted pathways where two of the three events are concerted while the third occurs separately and, ultimately, the case where all three events are concerted.

Although these "PCETBB/F" (proton-coupled electron transfer bond breaking/formation) reaction sequences are likely to be at work in a large number of catalytic or noncatalytic processes, examples where the mechanism has been firmly established are scarce. We discuss three of them in the following. The first one deals with the electrochemical reduction of an O–O bond in an organic peroxide with a pending carboxylic acid group. The second one

SCHEME 2[a]
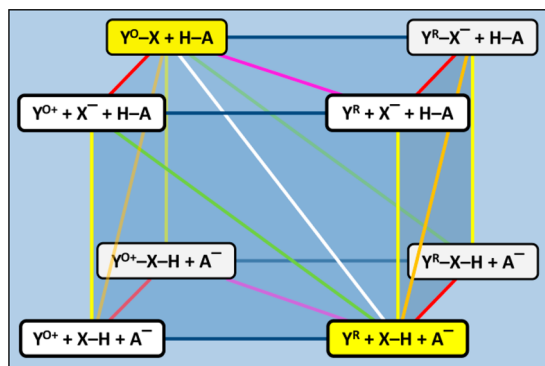
[a]Blue, electron transfer; yellow, proton transfer; red, bond breaking/formation; green, concerted proton−electron transfer; magenta, concerted bond breaking (/formation)−electron transfer; orange, concerted bond breaking (/formation)−proton transfer; white, all concerted.

concerns the key reaction of a catalytic cycle in which one of the C−O bonds of CO_2 is catalytically reduced to CO by means of an electrogenerated iron(0) porphyrins in the presence of a Brönsted acid. This case requires prior analysis of a relatively complex reaction sequence allowing the individuation of the reaction in which one of the C−O bound of CO_2 is broken by means of an intramolecular electron transfer coupled with proton transfer. The last example is also part of a catalytic process. It belongs to the vast category of reactions in which an electrogenerated low (or high)-valent metal coordination compound is used as catalyst, forming transitorily a complex with the substrate. Closing the catalytic loop then requires the breaking of a metal-heteroatom bond. In the example we discuss, a cobalt−carbon bond is cleaved by means of an electron transfer coupled with proton transfer. In the first two cases, the reaction follows an all-concerted pathway. It will thus be the occasion of describing a model of such reactions, which combines the previous model of concerted dissociative electron transfer with the model of concerted proton−electron transfer.

2. Proton-Coupled Electron Transfer Cleavage of an O−O Bond in the Electrochemical Reduction of an Organic Peroxide[28]

The effect of proton transfer coupling on the electron transfer triggered breaking of a O−O bond is illustrated by the comparison between the cyclic voltammetric responses of two aliphatic peroxide molecules, one of which contains a proximal carboxylic acid group while, in the other, the acid has been esterified (Figure 1). The most striking feature of this comparison is the considerable positive shift (700 mV) of the peak potential entailed by the presence of a neighboring
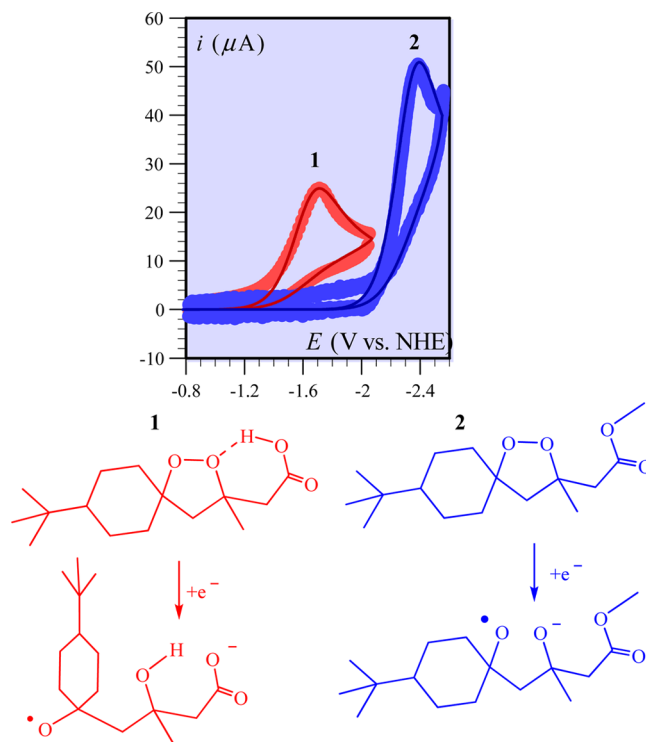

FIGURE 1. Comparative cyclic voltammetry of the two peroxides in DMF + 0.1 M *n*-Bu$_4$NBF$_4$ at 0.2 V/s, at a glassy carbon disk electrode. Thick lines: experimental. Thin lines: simulation (see last section).

acid group. That such a large shift points to an all concerted mechanism results from the following considerations. Aliphatic peroxides with no pendant acid groups undergo concerted dissociative electron transfer; that is, bond breaking is concerted with electron transfer.[29] The occurrence of pathways initiated by proton transfer is excluded by the lack of basicity of the peroxide moiety. A drastic simplification of the set of reaction pathways represented in Scheme 2 ensues, leading to the two possible pathways shown in Scheme 3. The stepwise pathway, electron transfer concerted with bond breaking (magenta) followed by proton transfer (yellow), can be easily ruled out: since the first step is irreversible, the additional driving force offered by the follow-up protonation should not have any effect on the cyclic voltammetric response contrary to experiment. These observations unambiguously establish the occurrence of the all-concerted pathway (white line), which benefits from a driving force advantage of 1.11 eV resulting from the difference in pK (in DMF) between the alcohol (32.4) and the carboxylic acid (13.3). The absence of a H/D kinetic isotope effect is also worth noting. We will be back to the modeling of this all-concerted type of reaction in the last section, leading to the satisfactory simulation of the experimental data shown in Figure 1.

SCHEME 3[a]
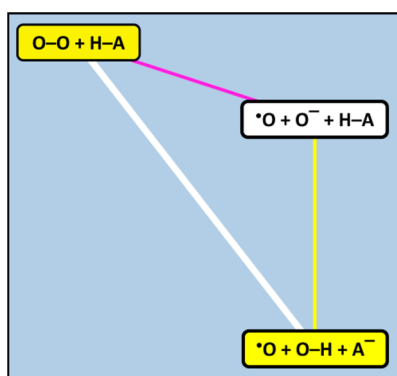
[a]Yellow, proton transfer; magenta, concerted bond breaking (/formation)-electron transfer; white, all concerted.

SCHEME 4

$$CO_2 + 2e^- + 2AH \longrightarrow CO + H_2O + 2 A^-$$
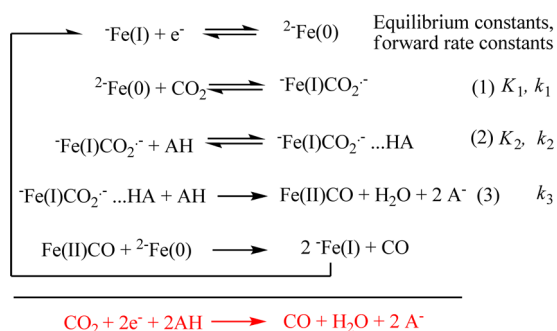
3. Cleavage of a C−O Bond in the Electrochemical Reduction of CO_2 Catalyzed by Electrogenerated Iron(0) Porphyrins Coupled with Proton Transfer

Focusing on the reduction of CO_2 to CO, a number of catalysts, mostly low oxidation states of transition metal complexes, have been proposed.[17] Among them, iron(0) porphyrins, electrochemically generated at a mercury or a glassy carbon electrode, are efficient, specific and durable catalysts provided they are coupled, in the framework of an electron-push−pull process, with Lewis acids or weak Brönsted acids.[30] The effect of four Brönsted acids −AcOH, PhOH, TFE (trifluoroethanol), H_2O− on the catalysis of CO_2 reduction to CO has recently been systematically analyzed in the aim of individuating the step −or steps− during which one of the C−O bonds of CO_2 is broken within the multistep catalytic sequence and determining the degree of concertedness of the association of bond breaking with proton and electron transfer,[31] leading, in the framework of Scheme 4, to the determination of the kinetic constants reported in Table 1 (a reminder of the procedures followed in this purpose is given in the Supporting Information).

TABLE 1. Kinetic Constants

AH	pK^a	K_1k_2 (M^{-2} s^{-1})	$K_1K_2k_3$ (M^{-3} s^{-1})	$K_1K_2k_3$ KIE
H_2O	31.5		10^2	
TFE	24.0		8×10^4	1.8
PhOH	18.8	4×10^4	8×10^6	2.5
AcOH	13.3	6×10^5	1.2×10^8	1.5

[a]See the Supporting Information.

SCHEME 5[a]
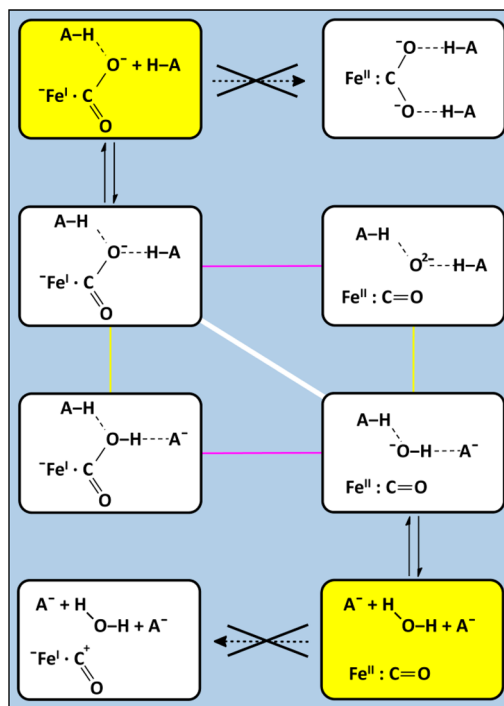
[a]Yellow, proton transfer; magenta, concerted bond breaking (/formation)-electron transfer; white, all concerted.

As regards the mechanism of reaction 3 (Scheme 4), the addition of the second molecule of AH involves the formation of a precursor complex in which a H-bond is formed between one of the oxygen of CO_2 and this second AH molecule. This adduct may take the two forms depicted on top of Scheme 5, which are in correspondence each with the following resonant forms of the initially formed CO_2 adduct, respectively:
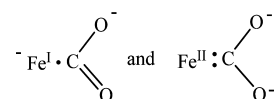
As depicted in Scheme 5, in the filiation of the general Scheme 2, the two possible forms of the precursor complex are correspondingly asymmetrical and symmetrical. The two carbon−oxygen bonds do not play a symmetrical role in the reaction, since one bond is broken during the

proton-coupled intramolecular electron transfer process while the other one is preserved in CO. It follows that the reaction involves the Fe^I asymmetrical adduct rather than the Fe^{II} symmetrical adduct. In the reverse reaction the precursor complex may also take two forms, corresponding to a Fe^I and a Fe^{II} resonant form: $^-Fe(I)\cdot{}^+C{=}O$ and $Fe^{II}{:}C{=}O$, respectively, thus giving rise to the two adducts shown at the bottom of Scheme 5, the reaction going through the Fe^{II} adduct rather than through the Fe^I adduct. The bond cleavage process may therefore be described as an intramolecular concerted dissociative electron transfer (CETBB) which may be concerted with proton transfer (CPETBB) or may follow the stepwise pathways represented in Scheme 5. It is possible to discriminate between the three pathways based on the variations of the kinetic constant $K_1K_2k_3$ with the pK of the added acid (Table 1). A linear correlation between log $K_1K_2k_3$ and the pK is found, with a slope of -0.35 (Figure 5S in the Supporting Information), which reflects the variation of log K_2k_3 with the pK since K_1, the equilibrium constant for the formation of the initial adduct between the iron(0) porphyrin and CO_2, is expected to be independent of the pK.

In view of the lack of correlation between H-bonding ability and pK,[32] K_2 may also be considered as approximately constant in the series. The linear correlation in Figure 5S (Supporting Information) with its -0.35 slope may therefore be viewed as a Brönsted relation between log k_3 and the acid pK. This observation rules out a mechanism in which a reversible proton transfer (PT) would precede a CETBB rate determining step in which case the Brönsted slope would be 1. If, conversely, in a PT+CETBB pathway, the initial proton transfer is not at equilibrium but is the rate determining step, then, because the anion radical of CO_2 is a strong oxygen base, its protonation is expected to be independent of the acid pK, being close to the diffusion limit. Consequently, the stepwise PT+CETBB pathway can be ruled out. The other stepwise pathway (CETBB + PT) in which, starting from the doubly H-bonded structure, bond cleavage would be the rate determining step followed by a fast protonation may also be dismissed. Indeed, this would involve the very improbable formation of an intermediate in which the oxygen atom would bear two negative charges.

It thus appears that the only viable pathway involves as rate determining step an electron transfer from the iron center concerted with proton transfer and C−O bond breaking (CPETBB, white pathway, Scheme 5). The experimental value of -0.35, clearly below -0.5, is typical of reaction in which bond breaking and electron transfer are concerted,[9,10] thus validating further the description of the

bond cleavage as an intramolecular dissociative electron transfer.

The concerted proton−electron transfer character of the CPETBB pathway is consistent with the H/D kinetic isotope effect found upon addition of hydrogenated and deuterated acids (Table 1). Modeling of this intramolecular concerted proton−electron transfer breaking of a carbon−oxygen bond is discussed in the last section. We also note that the boosting role of acids in the catalytic reduction of CO_2 to CO has recently been taken advantage of by installing phenolic groups on the porphyrin molecule resulting in the best and cheapest existing homogeneous catalyst today in terms of turnover frequency and overpotential.[33]

4. Cleavage of a Cobalt−Carbon Bond by Means of An Electron Transfer Coupled with Proton Transfer in the Catalysis of Chloroacetonitrile Reduction by Electrogenerated Cobalt(I) Porphyrins

Molecular catalysis of electrochemical reactions often involves, as in the preceding section, transition metal complexes. In these catalytic loops, the reductive or oxidative cleavage of a metal-heteroatom bond, for example, metal−oxygen or metal−carbon bond, is an essential step in the regeneration of the active form of the catalyst. In many cases, the latter reaction entails the coupling of electron and proton transfers. Three events are then associated: electron transfer, proton transfer, and bond breaking. The overall kinetics depends on the degree of concertedness between two or three of these three events as in the two preceding examples.

The question of proton−electron transfer bond cleavage of a metal−carbon bond in a catalytic process involving a transition metal complex has recently been addressed, taking as illustrating example the electrochemical reduction of an alkyl halide, chloroacetonitrile, catalyzed by electrogenerated cobalt(I) tetraphenylporphyrin (Co^ITPP).[34]

Cyclic voltammetry (Figure 2) shows a first wave where the $Co^{III}R$ (R $= CH_2CN$) complex is formed. The second wave is catalytic and involves a proton-coupled electron transfer cleavage of the cobalt−carbon bond.

In the general eight-cornered set of reaction pathways shown in Scheme 2, several possible intermediates may be dismissed as being of too high energy. This is the case for $^+Co^{III} + R^- + H - A$. Indeed, $Co^{III}R$ is stable with no tendency to split spontaneously, as results from cyclic voltammetry. The same is true for $Co^{III}-RH^+ + A^-$ since $Co^{III}R$ is also stable toward protonation. As regards $Co^{II}-RH + A^-$, $Co^{II}R$ is stable
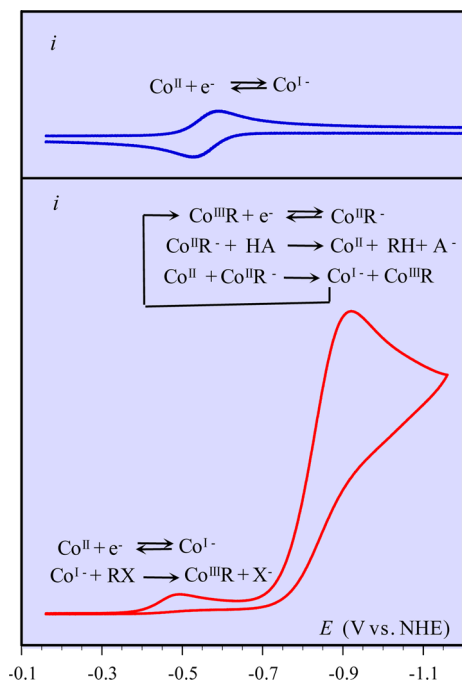
FIGURE 2. Cyclic voltammetry of $Co^{II}TPP$ (1 mM) in DMF + 0.1 M *n*-NBu$_4$ClO$_4$ in the absence (upper diagram) and presence (lower diagram) of 50 mM ClCH$_2$CN and 10 mM PhOH. Scan rate: 0.1 V/s. R = CH$_2$CN, X = Cl.

toward protonation as results from the observation that the electrons and the negative charge are delocalized in between the Co^{II} porphyrin and CH$_2$CN. In other words, Co^{II}–RH is not a viable intermediate between Co^{II}–R$^-$ + H − A and Co^{II} + RH + A$^-$. $^+$Co^{III} + R H + A$^-$ is much higher in energy than the final state since the $^+$Co^{III}/Co^{II} couple is ca. 0.35 V ahead of the catalytic wave. On total, the general scheme simplifies as represented in Scheme 6.

Systematic investigation of the catalytic current as a function of the concentration of the acid (phenol or acetic acid) revealed that the catalytic current increases with acid concentration until it levels off at a value dictated by the rate of production of Co^{III}R from the reaction of the cobalt(I) porphyrin with chloroacetonitrile. Starting from the simplified reaction sequence in Scheme 6, these observations allow ruling out several possibilities. In the completely stepwise mechanism (blue-red-yellow pathway in Scheme 6), the catalytic loop closing reaction (Co^{II} reduction) is so fast (at or close to the diffusion limit) that it outruns the backward cleavage reaction. The cleavage reaction is thus the rate-determining step, which renders the overall kinetics insensitive to the next protonation step. The overall rate constant should therefore be insensitive to the acid concentration contrarily to experimental facts, thus dismissing the possible occurrence of this pathway. If the mechanism would consist

SCHEME 6[a]
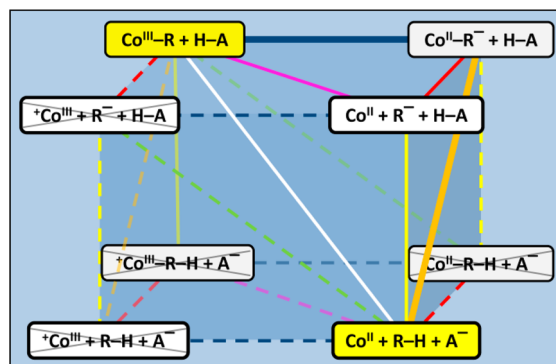
[a]Blue, electron transfer; yellow, proton transfer; red, bond breaking/formation; green, concerted proton−electron transfer; magenta, concerted bond breaking (/formation)−electron transfer; orange, concerted bond breaking (/formation)−proton transfer; white, all concerted.

of a concerted reductive cleavage followed by a protonation step (magenta-yellow pathway in Scheme 6), the protonation step, following an irreversible step, would have no influence on the overall kinetics. The observed strong variation of the catalytic current with the addition of acid thus rules out this mechanism. Finally the possible occurrence of a mechanism in which electron transfer, Co−C bond breaking, and proton transfer would be concerted (white pathway in Scheme 6) may be excluded for the following reasons. When, at large ClCH$_2$CN concentration, a plateau-shape is reached upon increasing acid concentration, the wave should shift toward positive potentials because the acid is then a reactant in the single-step termolecular reaction that involves, besides itself, the electrode, and ClCH$_2$CN. This is not observed experimentally, ruling out this last mechanistic possibility. It may thus be concluded that bond breaking and proton transfer are concerted but that electron transfer precedes this concerted step leading to the bold two-step blue-orange pathway in Scheme 6.

5. Modeling Concerted Proton− Electron-Bond Breaking (/Formation)

The acid-assisted cleavage of an O−O bond of an organic peroxide and of one C−O bond of CO$_2$ discussed above are the first clearly identified examples of an all-concerted pathway involving an electrochemical and an intramolecular electron transfer, respectively. Modeling of the kinetics may be obtained by combining the approaches that have been followed previously to model concerted dissociative electron transfer with no accompanying proton transfer,[9,10] on the one hand and the concerted proton−electron transfer (CPET) with no heavy-atom bond breaking on the other.[21,23,24]

Figure 3 provides an outline of the main principles to be used to model the reaction kinetics so as to derive the rate law and the accompanying governing parameters. As in the simple CPET case, two successive applications of the Born−Oppenheimer approximation, lead to define the transition state in terms of a heavy atom coordinate and the pre-exponential factor in terms of a proton displacement coordinate. Concerning the first of these, heavy atom reorganization involves the solvent molecules, the vibrations of reactant bonds not being cleaved in the reaction and, most importantly, the contribution of bond cleavage. Regarding the latter, it seems appropriate to use the same approximation for the potential energy curves as for concerted dissociative electron transfers with no accompanying proton transfers, i.e., a Morse curve for the reactants and a repulsive Morse curve for the products (equal to the repulsive part of the reactant Morse curve) as shown in Figure 3.

In the electrochemical case, a first approach consists in considering that among all the electronic states of the electrons in the electrode, only those located at the Fermi level contribute to the reaction. Then, the rate law of the irreversible all-concerted reaction is

$$\frac{I}{F} = Z_{het}^{3rd} \exp\left(-\frac{\Delta G_{het}^{\neq}}{RT} \right) \times [Y^O - X] \times [HA] \qquad (4)$$

with

$$\Delta G_{het}^{\neq} = \frac{\lambda_{het} + D}{4} \left[1 + \frac{F(E - E^0)}{\lambda_{het} + D} \right]^2 \qquad (5)$$

$[Y^O−X]$ and $[AH]$ are the concentrations of the indicated species at the electrode surface, I, the current density, E, the electrode potential. E^0 is the standard potential of the $Y^O−X + HA/Y^R + XH + A^-$ couple. D is the homolytic dissociation energy of the $Y^O−X$ bond. The reorganization energy, λ_{het}, includes the energy for solvent reorganization and internal reorganization in the $Y−X$ molecule, besides the cleavage of the bond. As in the case of simple CPET reactions, the pre-exponential factor, Z_{het}^{3rd}, reflects a combinations of factors characterizing the formation of the precursor complex, the degree of adiabaticity of electron transfer and the effect of proton tunneling at the transition state.

In the case where the proton donor is attached to the structure that bears the cleavable heavy-atom bond, as in the illustrating example discussed in the first section, eq 4 is
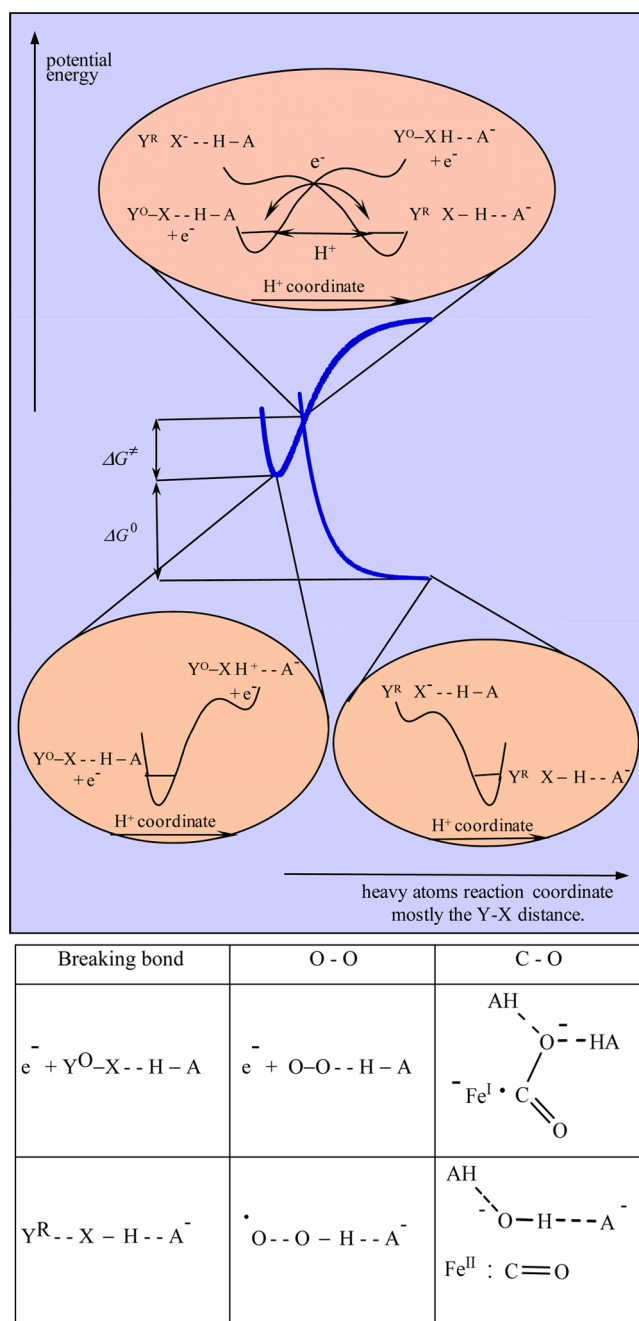

Breaking bond	O - O	C - O
$e^- + Y^O{-}X{-}{-}H{-}A$	$e^- + O{-}O{-}{-}H{-}A$	AH ⟍ O⁻ - - HA ⁄ $^-Fe^I \cdot C$ ⟍ O
$Y^R{-}{-}X{-}H{-}{-}A^-$	$\cdot O{-}{-}O{-}H{-}{-}A^-$	AH ⟍ O—H - - - A⁻ $Fe^{II} : C{=}O$

FIGURE 3. Potential energy curves for the reorganization of the heavy atoms of the system and for the proton displacement concerted with electron transfer (upper insert). Equivalence of the various states for the two reactions are defined in the above table.

replaced by a second order reaction rate law:

$$\frac{I}{F} = Z_{het}^{2nd} \exp\left(-\frac{\Delta G_{het}^{\neq}}{RT} \right) \times [Y^O - X, HA] \qquad (6)$$

with the same expression as in eq 5 for the activation free energy.

If all electronic states are taken into account, by analogy to the case of outersphere electron transfers, reaction 3 in

Scheme 4,[35,36] the rate law can be written as

$$\frac{I}{F} = \begin{matrix} Z_{het}^{3rd} \times [Y^O - X] \times [HA] \\ \text{or} \\ Z_{het}^{2nd} \times [Y^O - X, HA] \end{matrix}$$

$$\times \int_{-\infty}^{\infty} \frac{\exp\left[-\dfrac{RT}{4(\lambda_{het} + D)} \left\{ \dfrac{1}{RT}[(\lambda_{het} + D) + F(E - E^0)] - \zeta \right\}^2 \right]}{1 + \exp(\zeta)} d\zeta$$

$$(7)$$

In the proton-assisted dissociative electron transfer of the peroxides described in the first section, the attachment of the acid group to the molecule amounts to a very large local concentration of acid, spatially well located to partake in the all-concerted process. Addition of an external acid is inefficient in this purpose, the use of a very large concentration being impeded by its direct reduction at the electrode. In the application of the model to the reaction, the absence of H/D kinetic isotope effect may look surprising in view of the contribution of proton (/deuteron) tunneling in the value of the pre-exponential factor as in CPET reactions with no heavy-atom bond breaking where small but significant (of the order of 2) H/D kinetic isotope effects are commonly observed.[20,22,37] There is however an important difference between these reactions and the present ones, namely, the large irreversibility caused by the breaking of the heavy-atom bond, as pictured in Figure 3, which results in a larger reorganization energy due to the contribution of D. To overcome this intrinsic barrier, a large driving force is required. It follows that the transition state closely resembles the initial state. One consequence is that, in the heavy-atom transition state, the $Y^R X^-$ moiety is much less basic than in the products' geometry because the $Y - X$ bond is not completely broken. In the representation given in Figure 3, this situation results in the $Y^R X^- \cdots HA$ electronic state in the upper insert being very low in energy (lower than shown in the general case represented in the figure) so as to be close to the zero point energy level. The overlap of proton vibronic states is then large and therefore insensitive to isotope substitution.

The cyclic voltammetric responses of the acid- and ester-substituted peroxides (Figure 1) may be simulated by application of eqs 5 and 7, with the following parameters. The standard potential of **2** was equaled to the previously determined value for di-*tert*-butyl peroxide,[29] $E^0(\textbf{2}) = -1.24$ V vs NHE. The standard potential for **1** is then obtained by adding to $E^0(\textbf{2})$ the previously estimated increase in driving force deriving from proton transfer, thus resulting in $E^0(\textbf{1}) = -0.13$ V vs NHE. Simulation of the responses of **1** and **2** (Figure 1) with the same value of the pre-exponential factor

resulted in the following values: $Z_{het}^{2nd} = 0.1$ cm s^{-1}, $(\lambda_{het} + D) = 2.6$ eV. The fact that the difference between the peaks is 0.7 V instead of 1.1 V derives from a small interaction between the two oxygen in the esterified peroxides (see ref 28 for details, where the difference in peak heights is also explained as resulting from a "father-son" reaction taking place in the acid case and is absent in the ester case). The small value of the pre-exponential factor is, for the reasons given earlier, a reflection of the nonadiabaticity of electron transfer, a characteristic already noted with the reductive cleavage of other peroxides with no accompanying proton transfer. It is noteworthy that not only the location and height of the cyclic voltammetric responses of both compounds are correctly reproduced by the simulation but also their shape. In this connection, the difference between the peak and half-peak potentials indicates[36] a quite small transfer coefficient $\alpha = \partial\Delta G^{\neq}/\partial\Delta G^0 \approx 0.2$, which falls in line with the concerted character of the reaction and with the transition state closely resembling the initial state.

In the homogeneous case,

$$\text{rate} = k_{hom}^{3rd}[Y^O - X] \times [HA] \times [ED] \qquad (8)$$

(ED is the electron donor). Introducing the activation free energy, $\Delta G_{hom}^{\neq}$ and a third order pre-exponential factor, Z_{hom}^{3rd}, the rate constant may be expressed as

$$k_{hom}^{3rd} = Z_{hom}^{3rd} \exp\left(-\frac{\Delta G_{hom}^{\neq}}{RT} \right)$$

with

$$\Delta G_{hom}^{\neq} = \frac{\lambda_{hom} + D}{4} \left[1 + \frac{\Delta G^0}{\lambda_{hom} + D} \right]^2 \qquad (9)$$

where the driving force $-\Delta G^0 = F(E^0 - E_{ED}^0)$ (E^0 is the standard potential relative to the all-concerted reactionm, and E_{ED}^0 is the standard potential of the electron donor). λ_{hom} includes the solvent reorganization energy and the energy of internal reorganization in $Y^O - X$ and in ED molecule. As in the case of simple CPET reactions, the pre-exponential factor combines the formation of the precursor complex, the degree of adiabaticity of electron transfer, and the effect of proton tunneling at the transition state. The third order character of such reactions does not prevent their occurrence, as for example, in the homogeneous oxidation of phenol by Ru^{III}(bpy)$_3$ with hydrogen phosphate as the proton acceptor.[26] Systems where the proton donor or the electron donor is attached

to the structure that bears the cleavable heavy-atom bond, as in the example discussed in section 3, eq 8 is replaced by a second order reaction rate law:

$$\text{rate} = k_{\text{hom}}^{\text{2nd}} \times \begin{array}{c} [Y^O - X, HA] \times [ED] \\ \text{or} \\ [Y^O - X, ED] \times [HA] \end{array}$$

and are expected to be more efficient catalysts insofar the local concentrations of the attached HA or ED moiety are very large. Then

$$k_{\text{hom}}^{\text{2nd}} = Z_{\text{hom}}^{\text{2nd}} \exp\left(-\frac{\Delta G_{\text{hom}}^{\neq}}{RT} \right)$$

with the same expression of the free energy of activation as given by eq 9.

In view of the multistep character of the catalytic reaction discussed in section 3, the rate constant of the all-concerted reaction of interest (step 3 in Scheme 4) cannot be obtained separately from the prior steps 1 and 2. However, the kinetic effect of a variation in driving force may be gauged through the variation of the kinetic constant $K_1 K_2 k_3$ with the pK of the acids (Figure 5S) since the driving force of reaction 3 varies with the pK according to $\Delta\Delta G^0(3) = -(RT/F \ln10) \times \Delta pK$. From eq 9, it can be predicted that the symmetry factor of reaction 3 is approximately

$$\alpha(3) = \frac{1}{2}\left(1 + \frac{\Delta G_{\text{avg}}^0(3)}{\lambda_{\text{hom}} + D} \right) \approx 0.35$$

if it is assumed that K_2 does not vary very much from one acid to the other as expected from the lack of correlation between H-bonding and proton transfer basicity. This value of the symmetry factor, clearly below 0.5, falls in line with the concerted character of the reaction. The transition state thus resembles the initial state in this case too, but to a lesser extent than in the reduction of peroxides, in accordance with a small but non-negligible H/D kinetic isotope effect.[31]

6. Conclusions and Perspectives

The possibility of determining the degree of concertedness in proton-coupled electron transfer breaking of heavy atom bond has been illustrated by three different examples: electrochemical electron transfer breaking of an O−O bond in a molecule containing an acid group on the spot; breaking of one of the C−O bonds of CO_2 within a multistep intramolecular process using an electrogenerated iron(0) porphyrin as a catalyst, thus leading to CO; proton-assisted reductive cleavage of a cobalt−carbon bond within a multistep process using an electrogenerated an cobalt(I) porphyrin as a catalyst of the reduction of chloroacetonitrile. An all-concerted proton−electron-bond-breaking pathway prevails in the first two cases. In the third case, proton transfer and bond breaking are concerted after an initial electron transfer step. These are the first examples where the concerted vs stepwise character of the proton-coupled electron transfer breakings of heavy atom bond is unambiguously established. It may be expected that the strategies developed at this occasion will serve as guidelines in the future in the innumerable cases where the same question arises, having particularly in mind the activation of molecules involved in the modern energy challenges.

The advantage of concerted pathways is that they skip the high-energy intermediates involved in the stepwise pathways. However, this favorable thermodynamic situation may be counterbalanced by kinetic penalties. This is particularly likely in the reactions discussed here since they involve the breaking of a bond between heaving atoms. How these penalties can be fought by the supplement of driving force offered by the concertation with proton transfer is a correlative question. The kinetic model of the concerted proton-coupled electron transfer bond-breaking reaction that has been recently devised, based on previous dissociative electron transfer and CPET models, provides means to answer these questions.

Supporting Information. Kinetics of the reduction of CO_2 to CO catalyzed by iron(0) porphyrin. This material is available free of charge via the Internet at http://pubs.acs.org.

BIOGRAPHICAL INFORMATION

Cyrille Costentin received his undergraduate education at Ecole Normale Supérieure in Cachan. He is, since 2007, Professor at the University Paris Diderot. His interests include mechanisms and reactivity in electron transfer chemistry with particular recent emphasis on electrochemical and theoretical approaches to proton-coupled electron transfer processes.

Marc Robert was educated at the Ecole Normale Supérieure in Cachan. He is, since 2004, Professor at the University Paris Diderot. His interests include electrochemical, photochemical, and theoretical approaches of electron transfer reactions, as well as proton-coupled electron transfer processes in both organic chemistry and biochemistry.

Jean-Michel Savéant received his education in the Ecole Normale Supérieure in Paris. He is, since 1985, Directeur de Recherche au Centre National de la Recherche Scientifique at the University Paris Diderot. His current research interests involve all aspects of molecular and biomolecular electrochemistry as well as mechanisms and re-activity in electron transfer chemistry and biochemistry.

Cédric Tard studied chemistry at the University of Paris-Sud. He is currently a CNRS associate scientist at the University Paris Diderot. His research interests are centered on the synthesis of bioinspired molecules for electrochemical studies of proton-coupled electron transfer mechanisms.

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