

Transition between Concerted and Stepwise Dissociative Electron Transfers. An Example of How a Change of Temperature May Trigger a Change in Mechanism in Electrochemical Experiments

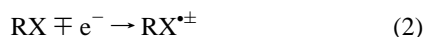
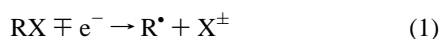
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Electron transfers involving the breaking of a bond may follow, in polar solvents, two distinct mechanisms. One in which the two events occur concertedly (reaction 1) and the other where electron transfer (reaction 2) and bond breaking (reaction 3) occur successively.¹



The question of the distinction and of the transition between the two mechanisms arises in electrochemical and bimolecular homogeneous reactions² and also in photoinduced reactions.³ On thermodynamic grounds, the passage from the stepwise to the concerted pathway is triggered by a decrease of the cleavage free energy of the ion radical, which may be segmented into three main quantities as shown in the following equation.²

$$\Delta G_{\text{RX}^{\bullet\pm} \rightarrow \text{R}^\bullet + \text{X}^\pm}^\circ = \text{BDFE} + E_{\text{RX}/\text{RX}^{\bullet\pm}}^\circ - E_{\text{X}^\bullet/\text{X}^\pm}^\circ$$

(BDFE is the RX homolytic bond dissociation free energy, and the E° are the standard potentials of the subscript couples.) How the molecular structure governs the occurrence of one or the other mechanisms through the variations of these three parameters has been illustrated by several experimental examples.^{1d,2,4}

The transition between the concerted and the stepwise mechanism may also be triggered by a change in the reducing (or oxidizing) power of the outersphere electron donor (or acceptor) opposed to the reactant, an electrode or an homogeneous reagent as sketched on Figure 1. The theoretical interest of providing evidence that such transitions can be experimentally observed resides in the demonstration that the concerted or stepwise character of a reaction is not related to the "existence"

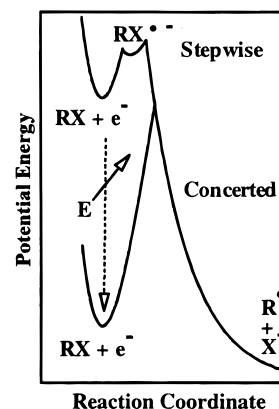


Figure 1. Transition between a stepwise and a concerted reductive cleavage mechanism as a function of the reducing power of the donor. E is the electrode potential for electrochemical reactions and the standard potential of the donor for homogeneous reactions. For oxidative cleavages, RX being the donor, E would be the oxidative power of the acceptor and the transition between stepwise and concerted mechanism would occur upon decreasing E .

or "non-existence"^{5a} of the intermediate, as often assumed in sake of simplification,^{5b} but is rather dictated by the lowest free energy pathway.

An early observation of the transition between the two mechanisms triggered by a variation of the reducing power of the donor was made with the homogeneous reductive cleavage of triphenylmethylphenyl sulfide (giving $\text{Ph}_3\text{C}^\bullet$ and PhS^-) by a series of anion radical.^{1c} Albeit small, the effect seems real even if some ambiguity arises from the fact that the reorganization energy may vary from one donor to the other in the series. In principle, electrochemical experiments are devoid from this ambiguity. The transition between the concerted and the stepwise mechanism has been observed in the electrochemical reductive cleavage of two sulfonium cations, $\text{Ph}(\text{CH}_3)\text{S}^+\text{CH}_2\text{Ph}$ and $\text{Naph}(\text{CH}_3)\text{S}^+\text{CH}_2\text{Ph}$ (yielding the benzyl radical and the corresponding sulfide), in acetonitrile.^{4c,6} The change in mechanism was observed by means of the peak width of the irreversible voltammetric wave, and, in all cases, the increase in the thermodynamic driving force was produced by an increase of the scan rate which shifts the voltammetric peak in the negative direction. The variations of the peak are small also (20 mV at maximum). It is thus worth trying to confirm the reality of the change in mechanism by other means.

We have found that a variation of the temperature may produce changes in the cyclic voltammetric wave that indeed confirm the mechanism transition. The example we selected is the electrochemical reduction of the sulfonium cation $\text{Ph}(\text{CH}_3)\text{S}^+\text{CH}_2\text{Ph}$ in acetonitrile. The cyclic voltammetric wave obtained at a glassy carbon electrode at 273 K is irreversible whatever the scan rate (from 0.1 to 100 V/s) as it is at 293 K. Figure 2a summarizes the variations of the peak width (i.e., the difference between the half-peak potential, $E_{p/2}$, and the peak potential, E_p) with the scan rate at the two temperatures. At 293 K, the transition between the concerted and stepwise

(5) (a) Meaning that the lifetime of the intermediate is larger or smaller respectively than one vibration of the cleaving bond. (b) See for example ref 5c. (c) Eldin, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1995**, *117*, 9415.

(6) (a) Some evidence has been provided that a similar phenomenon occurs in the reduction of $p\text{-EtOCOCHCHBrCH}_2\text{Br}$ in acetonitrile, although the reduction mechanism is complicated by follow-up reactions. (b) Another clear-cut example has been found recently involving the reduction of *tert*-butyl-*p*-cyanoperbenzoate in *N,N*-dimethylformamide where the convolution technique was employed.^{6c} A better precision than with peak-width measurements is thus reached owing to the use of a larger part of the information contained in each single voltammogram.^{6d} (b) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* In press. (d) Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1975**, *65*, 57.

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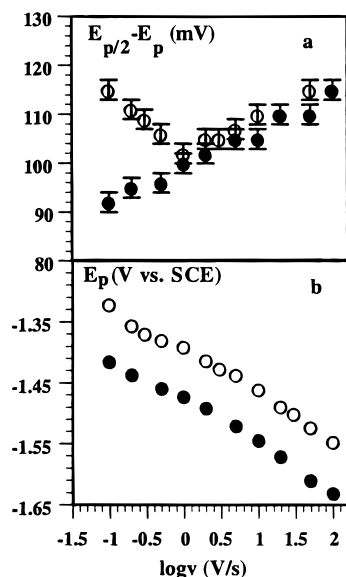


Figure 2. Cyclic voltammetry of the reduction of $[\text{Ph}(\text{CH}_3)\text{SCH}_2\text{Ph}]^+$ in acetonitrile + 0.1 M $n\text{-Bu}_4\text{NBF}_4$ at 293 (○) and 273 (●) K. The peak potential measurements were performed with a nonisothermal bridge⁹ connecting the cell to an SCE reference electrode maintained at 293 K. The error on the peak potential measurement (not shown on the figure) is ± 2 mV.

mechanism is revealed by the variation of the peak width upon increasing the scan rate. It decreases in the initial portion of the plot, then passes through a minimum, and finally increases. The concerted mechanism is followed at the lower end of the range of scan rates, while the stepwise mechanism is followed at the upper end.

When the temperature is decreased to 273 K, the variation of the peak width does not go any longer through a minimum but rather increases continuously from low to high scan rates.⁷ The values then observed are typical of a two-step mechanism in which the kinetic control passes progressively, as the scan rate increases, from the cleavage reaction (step 3 with step 2 acting as a preequilibrium) to the outersphere electron transfer (step 2).⁸ We may thus conclude that the stepwise mechanism is now followed over the whole range of scan rates.

Why does the decrease in temperature eliminate the occurrence of the concerted mechanism in the lower portion of the range of scan rates? The answer is provided by the examination of Figure 2b that shows the variations of the peak potential with the scan rate at the two temperatures. The reduction peak is systematically more negative at 273 K than at 293 K (by ca. 100 mV in average). It follows that more driving force is offered to the reaction at the former than at the latter temperature thus favoring the stepwise pathway at the expense of the concerted pathway. Why does the decrease in temperature render the peak more negative? At the lowest scan rate, for $T = 293$ K, an irreversible dissociative electron transfer takes place. At the peak, the rate balance between electrode reaction and diffusion may be expressed as¹⁰

$$\Delta G_p^\ddagger = \frac{RT}{F} \left\{ \ln \left[A \left(\frac{RT}{\alpha_p F v D} \right)^{1/2} \right] - 0.78 \right\} = \Delta G_0^\ddagger \left(1 + \frac{E_p - E^\circ}{4\Delta G_0^\ddagger} \right)^2$$

with

$$\alpha_p = 0.5 \left(1 + \frac{E_p - E^\circ}{4\Delta G_0^\ddagger} \right)$$

(R : gas constant, F : faraday, T : temperature, v : scan rate, D : diffusion coefficient, A : heterogeneous pre-exponential factor, ΔG_p^\ddagger and α_p : activation free enthalpy and transfer coefficient at the peak, ΔG_0^\ddagger : intrinsic barrier, E_p : peak potential, E° : standard potential). For a given scan rate and a given temperature, a fixed activation free energy is "seen" at the peak. Increasing the scan rate at a fixed temperature amounts to decreasing the activation free energy. Increasing the scan rate induces a negative shift of the peak potential and hence an increase of the driving force offered to the reaction. This is the reason that the transition between the concerted and the stepwise mechanism can be observed at 293 K upon raising the scan rate. At a fixed scan rate, decreasing the temperature induces the following negative shift of the peak potential, hence offering more driving force to the reaction.

$$\frac{\partial E_p}{\partial T} = \Delta S_0 + \frac{1}{\alpha_p} \frac{\partial}{\partial T} \left\{ \ln \left[A \left(\frac{RT}{\alpha_p F v D} \right)^{1/2} \right] - 0.78 \right\}$$

($\Delta S^\circ = \partial E^\circ / \partial T$ is the standard entropy of the reaction). The predominating contribution is $(R/\alpha_p F) \ln [A(RT/\alpha_p F v D)^{1/2}]$ leading to a negative shift of ca. 75 mV from 293 to 273 K. ΔS° is expected to be positive because both the cleavage and solvation entropies are positive (the reactant bears a positive charge while the products are neutral) thus increasing the driving force variation. Overall, the effect of decreasing the temperature is an increase of the driving force that favors the stepwise mechanism and thus makes the transition between the two mechanisms disappear.¹¹

We may thus conclude that the observed variations of the peak width with temperature provides a clear confirmation of the occurrence of a transition between concerted and stepwise mechanism in the reductive cleavage of the phenylmethylbenzyl sulfonium cation. Joining these results with those recently obtained in the electrochemical reduction of a completely different family of compounds, namely organic peroxides,^{6b,c} as well as with the earlier data pertaining to the homogeneous reductive cleavage of triphenylmethylphenyl sulfide^{1c} leads to the conclusion that transition between a concerted and a stepwise mechanism may indeed be triggered by an increase of the driving force offered to the reaction thus following the theoretical expectations summarized in Figure 1.

From a methodological standpoint, the results and their analysis show that changing temperature may help, in addition to changing concentrations and scan rate, to elucidate rather subtle changes in mechanism in the cyclic voltammetric analyses of electrochemical reactions.

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(7) (a) At both temperature, the overall electron stoichiometry is 1, corresponding to the rate determining formation of the benzyl radical followed by its reduction into the carbanion which eventually abstracts a proton from the starting molecule yielding the ylid.^{4c} (b) α can also be derived from the slope of the $E_p - \log v$ plots,⁸ albeit with less precision. The values thus found agree with those obtained from the peak width.

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(11) As the mechanism changes upon increasing the driving force, the variation of the peak potential depicted by eq 1 is less and less rigorously exact. At the lower end of the temperature range the kinetics of the electrode reaction are controlled by steps 2 and 3. The peak shift for a pure kinetic control by step 2 obeys the same equation with slightly different values of α_p and ΔS° . For a pure kinetic control by step 3, $E_p = E_3^\circ + (RT/2F) \ln (RTk_3/Fv)$. Decreasing temperature again results in a negative shift of the peak potential in this case as in all the other cases.