PCCP

www.rsc.org/pccp

COMMUNICATION

Reorganization energy and pre-exponential factor from temperature-dependent experiments in electron transfer reactions. A typical example: the reduction of *tert*-nitrobutane

Cyrille Costentin, Cyril Louault, Marc Robert, Vincent Rogé and Jean-Michel Savéant*

The electrochemical one-electron reduction of *tert*-nitrobutane in *N,N′*-dimethylformamide is a typical reaction, which has been shown to follow the quadratic model of outersphere electron transfer. The variation of the standard rate constant with temperature allows a separate determination of the reorganization energy and of the pre-exponential factor. The value found for the former is in agreement with independent estimates of the solvent and intramolecular reorganization energies. The value of the latter, significantly larger than the collision frequency, implies that the reaction starts to take place before close contact with the electrode surface.

Considerable attention is currently devoted to proton-coupled electron transfers in view of their ubiquity in natural systems on the one hand and in activation of small molecules involved in the resolution of modern energy challenges on the other.[1] Particular emphasis has been put in this area on concerted processes (CPET: concerted proton–electron transfer). In the various attempts to develop and test a theoretical model of the electrochemical CPET reactions, attention has been called to the usefulness of a full analysis of the kinetics of simple outersphere electron transfer reactions, which may serve further on as references for the more complicated cases of CPET reactions (see for example ref. 2). As detailed below the reduction of *tert*-nitrobutane in *N,N′*-dimethylformamide at a mercury electrode appears as such a system, the kinetic analysis of which is worth completing adding new experiments and treatments to the already available data. In this respect, determination of both reorganization energy and pre-exponential factor is crucial in order to have benchmarks to compare simple outersphere electron transfer and CPET processes.

Kinetic models of outersphere[3] electron transfer, based on a quadratic dependence of the activation free energy $\Delta G_f^{\neq}$, from the driving force, $-\Delta G^0$ (eqn (1)), are available since a long time.[4,5]

$$\Delta G_f^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \qquad (1)$$

Univ Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS, 15 rue Jean-Antoine de Baïf, F-75205 Paris Cedex 13, France. E-mail: saveant@univ-paris-diderot.fr

where λ is the reorganization energy. The forward electron transfer rate constant, k_f, is then given by:

$$k_f = Z \exp\left(-\frac{\Delta G_f^{\neq}}{RT}\right) \qquad (2)$$

where Z, the pre-exponential factor, is a measure of the approach between the reactants and the adiabaticity of the electron transfer.

In the electrochemical case,

$$\Delta G^0 = F(E - E^0)$$

for reduction and the applicability of eqn (1) and (2) requires the approximation that electron electronic states in the electrode involved in the reaction are those belonging to the Fermi level.

In spite of the longstanding availability of the Marcus–Hush model, detailed experimental testing of the quadraticity of the activation–driving force relationship and determination of the kinetic-governing parameters are scarce. Assuming *a priori* the validity of the Marcus–Hush model, the reorganization energy, considered to arise essentially from solvent reorganization, was determined in a large series of aromatic molecules, based on the assumption that the pre-exponential factor is equal to the collision frequency.[6] The quadratic character of the activation–driving force law (eqn (1)) resulting in a linear variation of the transfer coefficient, α (eqn (3)), has then been shown to be valid for the one-electron reduction of *tert*-nitrobutane in *N,N′*-dimethylformamide (DMF) and acetonitrile (ACN) on mercury[7] and platinum electrodes.[8]

$$\alpha = \frac{\partial \Delta G_f^{\neq}}{\partial \Delta G^0} = \frac{\partial \Delta G_f^{\neq}}{\partial E} = \frac{1}{2}\left(1 + \frac{\Delta G^0}{\lambda}\right) = \frac{1}{2}\left(1 + \frac{F(E - E^0)}{\lambda}\right) \qquad (3)$$

Similar conclusions were drawn for the reduction of other organic molecules (nitromesitylene, nitrodurene, terephthalonitrile, phthalonitrile, diacetyl benzene) in ACN, although the variation of the transfer coefficient with driving force could be observed on a narrower range of electrode potential.[9] The same demonstration has also been made for the reduction of benzaldehyde in ethanol.[10] It was emphasized that the choice of uncharged molecules to investigate the variation of α with potential minimized the double layer effects as compared to attempts

using charge metal complexes, with which α variations may be blurred by the potential dependence of double layer effects. In all these cases, the reorganization energy was derived from the experimental data by means of eqn (1) and (2), taking for the pre-exponential factor, Z, the frequency for the collision of the reactant with the electrode surface.[11] Recent theoretical developments have drawn attention on the possibility that the reactant may react at larger distances than close contact, which results in a larger value of the pre-exponential factor.[2,12]

One way for determining the pre-exponential factor and the reorganization energy separately is to observe the variation of the electrochemical kinetics with temperature. The electrochemical reduction of *tert*-nitrobutane on a mercury electrode in N,N'-dimethylformamide was selected as an example since the quadratic character of the rate law was thoroughly ascertained in this case. The values of both the reorganization energy and pre-exponential factor will be compared to theoretical estimations.[13]

Typical cyclic voltammetric responses obtained as a function of temperature are shown in Fig. 1. They can be simulated by linearizing the current–potential relationship at the electrode surface so as to treat the data by a Butler–Volmer law with a transfer coefficient equal to 0.5, as justified by the rather limited extent of the potential excursion and by the thickness (difference between the half peak and the peak potentials) of the voltammetric waves. The experimental curve could thus be simulated[14] satisfactorily leading to the standard rate constants, k_S, displayed in Fig. 2.

The Arrhenius plot in Fig. 2 may be expressed as:[14e]

$$\ln k_S = \ln Z - \left(\frac{\lambda}{4} + \frac{F}{2}\phi_S\right)\frac{1}{RT}$$
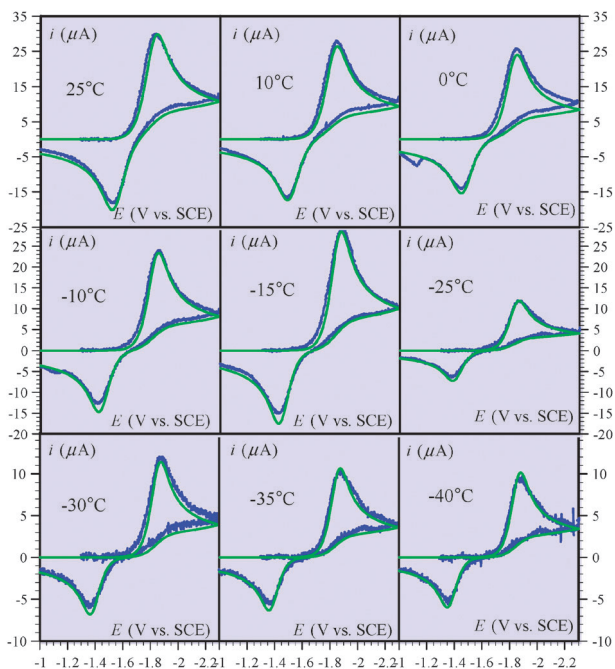
Fig. 1 Cyclic voltammetry of *tert*-nitrobutane (1 mM) in DMF + 0.1 M n-NBu$_4$BF$_4$ on a mercury drop electrode (the size of the drop is not the same in all experiments) as a function of temperature (as indicated in each diagram). Scan rate: 10 V s^{-1}.[15–17] Blue: experimental curves. Green: simulated curves.
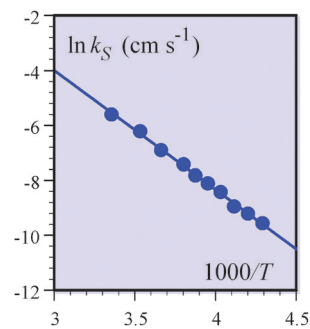
Fig. 2 Variation with temperature (K) of the standard rate constant derived from the simulations in Fig. 1, leading to the Arrhenius plot represented by the blue straight line.

where ϕ_S is the potential at the reaction site. From the linear fit in Fig. 2, it follows that $\lambda + 2F\phi_S = 1.5$ eV and $Z = 8350$ cm s^{-1}. ϕ_S may be approximated by the potential in the outer Helmholtz plane, *i.e.* $\phi_S = -0.12$ V.[6,9] It follows that $\lambda = 1.74$ eV.

Although this is not central to the purpose of establishing the kinetic parameters of our reference system, λ may be dissected into solvent reorganization energy, λ_0, and intramolecular reorganization energy λ_i. As discussed earlier, the solvent reorganization energy may approximately be estimated by the following relationship:[14e]

$$\lambda_0(\text{eV}) \cong \frac{3}{a(\text{Å})} = 1$$

where a is the radius of the reactant equivalent sphere, taking $a = 3$ Å, as estimated for the solvation radius of the nitro-portion of *tert*-nitrobutane where charge is located. Although more rigorous treatments have been developed,[18] a simple approximate quantum mechanical calculation (B3LYP/6-31 + G*[19]) allowed an estimation of λ_i according to the method depicted in Fig. 3, with:[20]

$$\lambda_i = \frac{[E_R(1) - E_R(0)] + [E_P(0) - E_P(1)]}{2}$$

As to the pre-exponential factor, $Z = 8350$ cm s^{-1}, it is significantly larger than the collision frequency,
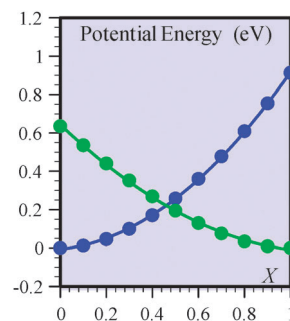
Fig. 3 Determination of λ_i. Potential energy as a function of a reaction coordinate X for *tert*-nitrobutane (blue), noted $E_R(X)$, and *tert*-nitrobutane anion radical (green), noted $E_P(X)$, in gas phase[21] leading to an average value of 0.73 eV. Adding the value of λ_i, thus found, to the preceding value estimated for λ_0 results in a value of λ equal to 1.73 eV, which compares very favorably with the experimental value, 1.74 eV. This excellent agreement is however partly fortuitous in view of the uncertainty embodied in the quantum chemical calculations. The important point is that the orders of magnitude are the same.

1582 | *Phys. Chem. Chem. Phys.*, 2012, **14**, 1581–1584

This journal is © the Owner Societies 2012

$Z = \sqrt{RT/2\pi M} = 6000$ cm s^{-1} (M: molar mass). The fact that the pre-exponential factor is larger than the collision frequency indicates that the reaction starts before close contact with the electrode surface, even though its probability is a decreasing function of the distance to the electrode surface.[2,12] The difference between the two values is however modest, owing to the large size of the n-NBu$_4^+$ cation of the supporting electrolyte, which renders the coupling between the reactant and the electrode inefficient for distances larger than the n-NBu$_4^+$ radius. This falls in line with a previously established correlation between the pre-exponential factor and radius of the supporting electrolyte cation, observed with the reduction of nitromesitylene in DMF.[13b] The electron transfer is thus in the non-adiabatic regime with an intrinsic coupling constant (electronic coupling constant between the electrode and the substrate at a nil approach distance) of *ca.* 0.12 eV.[22]

In summary, taking as an example the electrochemical one-electron reduction of *tert*-nitrobutane in DMF, a reaction which has been previously shown to obey the quadratic laws of outersphere electron transfer, the systematic investigation of the temperature dependence of the standard rate constant allows the separate determination of the reorganization energy and of the pre-exponential factor. Independent estimate of the reorganization energy from its outer and inner components is in good agreement with the experimental value. The pre-exponential factor is larger than the collision frequency, pointing to the fact that the reaction starts before close contact with the electrode surface. The large size of the supporting electrolyte cation, n-NBu$_4^+$, renders however this effect rather modest.

Notes and references

1 (a) C. Costentin, M. Robert and J.-M. Savéant, *Chem. Rev.*, 2010, **110**, PR1–PR40; (b) C. Costentin, M. Robert and J.-M. Savéant, *Acc. Chem. Res.*, 2010, **43**, 1019–1029; (c) J. Bonin, C. Costentin, M. Robert, J.-M. Savéant and C. Tard, *Acc. Chem. Res.*, DOI: http://dx.doi.org/10.1021/ar200132f.

2 (a) C. Costentin, M. Robert and J.-M. Savéant, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13061–13069; (b) C. Costentin, V. Hajj, C. Louault, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 2011, **133**, 19160–19167.

3 (a) Single electron transfers may be categorized as outersphere and innersphere processes according to whether they are not or whether they are accompanied in a concerted manner with breaking or formation of bonds. The classification originates from the electron transfer chemistry of metallic complexes,[3b] making a distinction between the reactions where one electron but no ligand is transferred and those where a ligand is transferred concertedly with one electron, which amounts for the transfer of an atom (or of a group of atoms). The notion was extended afterwards[3c] according to the definition above so as to include all kinds of molecules, including organic molecules; (b) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086–1094; (c) J.-M. Savéant, Single Electron Transfer and Nucleophilic Substitution, in *Advances in Physical Organic Chemistry*, ed. D. Bethel, Academic Press, New York, 1990, vol. 26, pp. 1–130.

4 (a) R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966–978; (b) R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679–701; (c) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta, Bioenerg.*, 1985, **811**, 265–322.

5 (a) N. S. Hush, *J. Chem. Phys.*, 1958, **28**, 962–972; (b) N. S. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557–580.

6 H. Kojima and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 6317–6324.

7 J.-M. Savéant and D. Tessier, *J. Electroanal. Chem.*, 1975, **65**, 57–66.

8 D. A. Corrigan and D. H. Evans, *J. Electroanal. Chem.*, 1980, **106**, 287–304.

9 J.-M. Savéant and D. Tessier, *Discuss. Faraday Soc.*, 1982, **74**, 57–72.

10 J.-M. Savéant and D. Tessier, *J. Phys. Chem.*, 1978, **82**, 1723–1727.

11 (a) Another approach deals with reactants anchored to the electrode surface. This strategy was applied to the reduction of ferrocene attached to the electrode surface by a long chain.[11b] The pre-exponential factor is then much smaller than in the preceding cases, because of electron tunneling over a large distance. The small value of Z thus allows its determination together with its organization energy at a given temperature. The validity of the Hush–Marcus kinetic law could then be tested after introduction of the contribution of all electronic states of electrons in the electrode, which wipes out the inverted region predicted by eqn (1)[11c]; (b) C. E. D. Chidsey, *Science*, 1991, **251**, 919–922; (c) V. G. Levich, Present State of the Theory of Oxidation–Reduction in Solution (Bulk and Electrode Reactions), in *Advances in Electrochemistry and Electrochemical Engineering*, ed. P. Delahay and C. W. Tobias, Wiley, New York, 1955, pp. 250–371.

12 S. W. Feldberg and N. Sutin, *Chem. Phys.*, 2006, **324**, 216–225.

13 (a) Two other determinations of the reorganization energy from temperature variations have been reported, assuming the validity of the Marcus–Hush model[13b,c]; (b) W. R. Fawcett, M. Fedurco and M. Opallo, *J. Phys. Chem.*, 1992, **96**, 9959–9964; (c) J. P. Bullock, E. Mashkina and A. M. Bond, *J. Phys. Chem. A*, 2011, **115**, 6493–6502.

14 (a) Using the DigElch software[14b]; (b) M. Rudolph, *J. Electroanal. Chem.*, 2003, **543**, 23–39; (c) Simulations of such transfer/diffusion controlled current–potential responses so as to access the standard rate constant are based on a dimensionless formulation of the diffusion–reaction problem, which may appear as governing parameter: $k_S(RT/FvD)^{1/2}$ (v: scan rate, D: reactant diffusion coefficient) indicating that large rate constants require large scan rates and *vice versa*.[14d,e] Since the standard rate constants are not very high (see Fig. 2), the scan rate need not be very high (see Fig. 1); (d) L. Nadjo and J.-M. Savéant, *J. Electroanal. Chem.*, 1973, **48**, 113–145; (e) J.-M. Savéant, *Elements of Molecular and Biomolecular Electrochemistry*, Wiley-Interscience, New York, 2006, ch. 1; (f) Accuracy was ±30%.

15 (a) *Chemicals: tert*-nitrobutane (Aldrich, 99%) and DMF (Fluka, > 99.5%, stored on molecular sieves under an argon atmosphere) were used as-received. NBu$_4$BF$_4$ (Fluka, puriss) was recrystallized twice from ethanol. *Instrumentation:* the working electrode was a hanging drop mercury (Aldrich, 99.9995%, filtered before use) electrode. The counter-electrode was a platinum wire and the reference electrode an aqueous saturated calomel electrode (SCE). The potentiostat, equipped with a positive feedback compensation and current measurer, was the same as previously described.[15b] Ohmic drop was carefully compensated. The solution was deoxygenated by bubbling argon prior to each experiment and an argon flow was kept over the solution during the whole experiment. Baselines were systematically recorded and subtracted. The double-wall jacketed cell was thermostated by circulation of 2-propanol, and the exact temperature inside the electrochemical cell measured; (b) D. Garreau and J.-M. Savéant, *J. Electroanal. Chem.*, 1972, **35**, 309–331.

16 (a) The diffusion coefficient was taken to be equal to 1.3 × 10^{-5} cm^2 s^{-1} at 20 °C,[16b] and assumed to increase by 2% per degree; (b) M. E. Peover and J. S. Powell, *J. Electroanal. Chem.*, 1969, **20**, 427–433.

17 Another set of experiments was carried out at 100 V s^{-1} leading to the same values of k_S.

18 A. Warshel and W. W. Parson, *Q. Rev. Biophys.*, 2001, **34**, 563–679.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi,

R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.

20 (*a*) Several methods based on the same principles have been proposed and applied at various levels of calculation[20b–d]; (*b*) S. F. Nelsen, S. C. Blackstock and Y. Kim, *J. Am. Chem. Soc.*, 1987, **109**, 677–682; (*c*) S. Jakobsen, K. V. Mikkelsen and S. U. Pedersen, *J. Phys. Chem.*, 1996, **100**, 7411–7417; (*d*) C. Costentin, M. Robert, J.-M. Savéant and C. Tard, *Phys. Chem. Chem. Phys.*, 2011, **13**, 5353–5358.

21 X is taken as the index of the reaction progress, varying between 0 and 1. X is a parameter interpolating the geometry of the reactant and the geometry of the product, therefore the variation of all intrinsic coordinates is taken into account in the reaction coordinate. Each intrinsic coordinate of the molecule, R_j, is assumed to vary linearly from its value in the reactant, $R_{j,X=0}$, to its value in the product, $R_{j,X=1}$: $R_j(X) = R_{j,X=0} + (R_{j,X=1} - R_{j,X=0})X$. Once all the $R_{j,X=0}$ (*tert*-nitrobutane) and $R_{j,X=1}$ (*tert*-nitrobutane anion radical) values have been determined by geometry optimization (B3LYP/6-31 + G*), the energies ($E_R(X)$ and $E_P(X)$) are calculated for a series of X values, leading to the quadratic variation shown in Fig. 3. This quadratic variation indicates that the use of a variation of each intrinsic coordinate at the same pace along the reaction coordinate does correspond to an apparent single quadratic mode.

22 See Fig. 4 and corresponding text in ref. 2a.