

Reorganization energies and pre-exponential factors in the one-electron electrochemical and homogeneous oxidation of phenols coupled with an intramolecular amine-driven proton transfer†

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Temperature variations of the kinetics of the electrochemical and homogeneous oxidation of the title compounds give rise to Arrhenius plots, the slopes of which give access to the heavy-atom (including solvent) reorganization energies. Information on the role of proton transfer in the dynamics of the concerted proton–electron transfer reaction (CPET) is potentially contained in the pre-exponential factor. Previous analyses of the problem were based on equalling the pre-exponential factor in the absence of barrier for proton transfer with the collision frequency. Taking into account that the reaction may take place at various distances from the electrode surface increases the value of this limiting pre-exponential factor. Strategies are discussed for evaluating the impact of proton transfer in the CPET kinetics by comparing the experimental pre-exponential factor with pre-exponential factors characterizing simple outersphere electron transfers.

1. Introduction

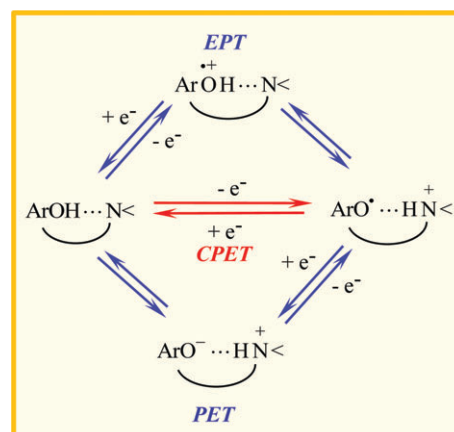
Proton-coupled electron transfers (PCET) are ubiquitous in natural and artificial chemical processes. The mechanisms and kinetics of these reactions where proton and electron transfer involves different molecular centers currently attract active attention with particular emphasis on the possibility that the two steps be concerted giving rise to CPET (concerted proton–electron transfer) reactions as opposed to stepwise pathways in which proton transfer precedes (PET) or follows (EPT electron transfer (Scheme 1). Among the natural processes, where PCET plays an important role, Photosystem II is the most emblematic example, concerning particularly the reaction in which electron transfer from tyrosine_Z is associated with proton transfer to histidine 190 (Scheme 2). Mimics of the tyrosine–histidine system of the type shown in Scheme 3 have been synthesized.¹ The kinetics of the electrochemical oxidation of **1**^{2,3} and of the homogeneous oxidation of **2** and other similar amino-phenols^{4,5} have been characterized, pointing to the predominance of the CPET pathway.

The treatment of the electrochemical kinetic data,^{3,9} based on the ideas developed in ref. 10 for proton transfer, involved a double application of the Born–Oppenheimer approximation taking into account that proton and electron are light particles as compared to the heavy atoms in the solvent and the reactants, whose configuration is reorganized during the CPET reaction; electron is a light particle as compared to proton. As discussed below the resulting electrochemical

oxidation rate law, relating the current, i , to the electrode potential, E , may be expressed as a Butler–Volmer relationship with a 0.5 transfer coefficient:¹¹

$$\frac{i}{FS} = k_S^{\text{het,ap}} \exp\left[\frac{F}{2RT}(E - E^0)\right] \times \left\{ [\text{red}] - \exp\left[-\frac{F}{RT}(E - E^0)\right] [\text{ox}] \right\} \quad (1)$$

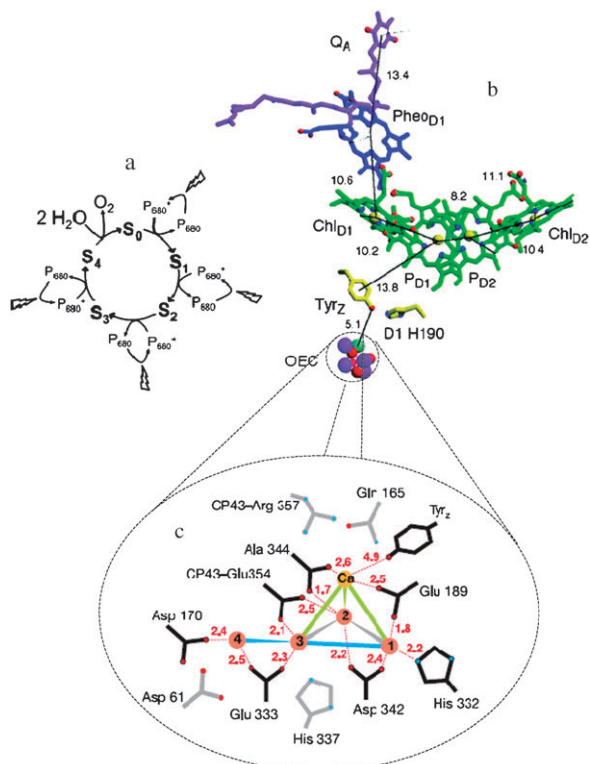
E^0 is the standard potential of the redox couple. S is the electrode surface area. The concentrations of reductant and oxidant at the electrode are given by $[\text{red}]$ and $[\text{ox}]$. $k_S^{\text{het,ap}}$ is the apparent standard rate constant, *i.e.*, the rate constant for $E = E^0$ (we will come back to the distinction between true and apparent standard rate constants later on) and is given by



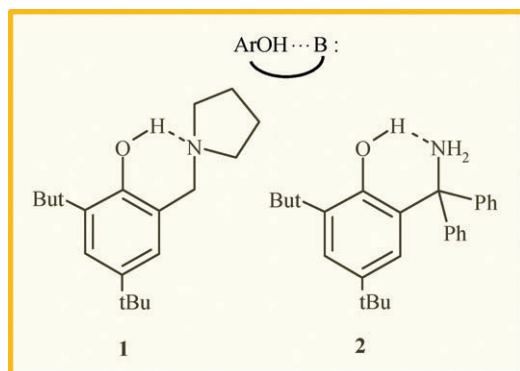
Scheme 1 PCET oxidation of a phenol ArOH bearing an attached proton acceptor, B. Concerted (red) and stepwise (blue) pathways.

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Scheme 2 Schematic view of Photosystem II. (a) Kok cycle.⁶ (b) Structure of the reaction center of Photosystem II showing the TyrZ-ChlD1(P680)-PheoD1-QA donor-chromophore-acceptor system, electron transfer from tyrosine (TyrZ) being coupled to proton transfer from histidine D1 H190 (the numbers are the distances in angstroms). OEC, oxygen evolving complex.⁷ (c) One proposed schematic view of the OEC Mn_4Ca_8 . Ala, alanine; Arg, arginine; Asp, aspartate; Glu, glutamate; His, histidine. The numbers are the distances in angstroms. In the labeling scheme, amino acids in black are in the first coordination sphere and those beyond in gray.



Scheme 3 The two amino-phenols the electrochemical (1) and homogenous (2) oxidation of which have been kinetically characterized in the framework of CPET reactions, serving as example in the present re-examination of reorganization energies and pre-exponential factors.

(definitions of all symbols are given in the Glossary of Symbols, at the end of this article).¹²

$$\ln k_S^{\text{het,ap}} = \ln(Z^{\text{het}}) - \left(\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\neq} - \frac{\Delta ZPE}{2} \right) \frac{1}{RT} \quad (2)$$

ϕ_S is the potential difference between the reaction site and the solution. ΔZPE^{\neq} is the difference between the zero-point energies of the H vibration at the transition state and at the reactant state. ΔZPE is the difference between the zero-point energies of the H vibration of the product state and the reactant state. The main term in the slope of the Arrhenius plot defined by eqn (2) is the heavy-atom reorganization energy, λ^{het} . In previous analyses of the electrochemical oxidation, Z^{het} , contained two factors. One, k_{∞}^{het} , is the rate constant that would be reached in the absence of heavy-atom reorganization and absence of barrier for proton-tunneling, whereas χ_{el} , the transmission coefficient is a measure of electronic states coupling which is related to proton tunneling and, as such, a key factor of the CPET reaction that defines its degree of adiabaticity. k_{∞}^{het} was equalled to the collision frequency, $k_{\text{coll}}^{\text{het}}$, times a factor

$$\frac{\pi}{\sqrt{1 + \pi RT/\lambda^{\text{het}}}} \sqrt{\frac{RT}{4\pi\lambda^{\text{het}}}} \simeq \pi \sqrt{\frac{RT}{4\pi\lambda^{\text{het}}}}$$

accounting for multi-electronic states in the electrode.^{2,3} This formulation implicitly assumed that the reaction takes place at a given distance from the electrode. A more realistic analysis should take into account the fact that the CPET reaction may take place at various distances from the electrode surface similarly to what happens with simple outersphere electron transfer reactions as mentioned long time ago^{13–15} and recently re-emphasized by several authors.^{16–18}

The main purpose of the present contribution is to estimate the values of the pre-exponential factor that should replace

$$\chi_{\text{el}} k_{\text{coll}}^{\text{het}} \frac{\pi}{\sqrt{1 + \pi RT/\lambda^{\text{het}}}} \sqrt{\frac{RT}{4\pi\lambda^{\text{het}}}}$$

and discuss the implications of this more realistic estimation in terms of degree of adiabaticity of the reaction and of reorganization energy, illustrated by the oxidation of 1. Similar questions arise in the case of homogeneous oxidation and will be discussed, taking as example the oxidation of 2.

2. Arrhenius plots

2.1 Electrochemical oxidation of 1

The standard rate constant for the oxidation of 1, k_S^{het} , has been previously experimentally determined as function of temperature assuming a Butler-Volmer kinetic law relating the current density to the potential.³ The validity of this law will be discussed later on in the framework of the improved treatment we are putting forward here. We will see that the standard rate constant has the classical form given in eqn (2), *i.e.* the product of a pre-exponential factor, henceforth designated by Z^{het} , whose temperature dependence is negligible and of an exponential term. A linear classical Arrhenius plot is obtained upon plotting the experimental standard rate constants against $1/T$ (Fig. 1). From the slope we obtain $\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\neq} - \frac{\Delta ZPE}{2} = 0.386$ eV and from extrapolation at infinite temperature we obtain $Z^{\text{het,CPET}} = 34580$ cm s⁻¹. The same analysis, repeated with compound 1 deuterated on the phenolic position leads to

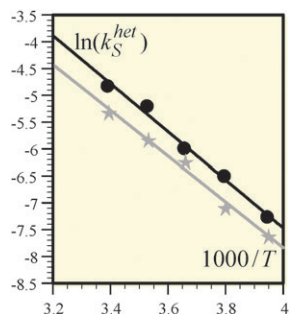


Fig. 1 Arrhenius plots for the oxidation of **1** in the presence of 2% CH₃OH (black dots) and of 2% CD₃OD (grey stars). Data from ref. 3. k_S^{het} in cm s⁻¹, T in K.

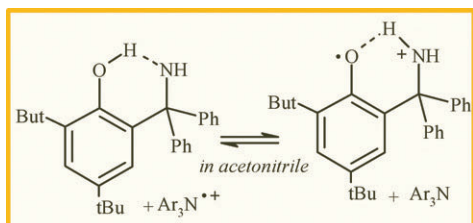
$\frac{\lambda_D^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE_D^\ddagger - \frac{\Delta ZPE_D}{2} = 0.368$ eV and $Z_D^{\text{het,CPET}} = 9985$ cm s⁻¹ in which the subscript D indicates that experiments have been performed in presence of 2% CD₃OD allowing complete deuteration of the phenol group. Taking $\Delta ZPE^\ddagger - \frac{\Delta ZPE}{2} = -0.04$ eV, ($\Delta ZPE_D = \Delta ZPE/\sqrt{2}$),³ $F\phi_S = 0.12$ eV,¹⁹ the reorganization energy ensues: $\lambda^{\text{het}} = 1.465$ eV ($\lambda_D^{\text{het}} = 1.34$ eV).

2.2 Homogeneous oxidation of 2

Oxidation of **2** by a series of triarylamine cation radicals (Scheme 4) led to the conclusion that the reaction is mildly nonadiabatic.⁵ Treatment of these data was further improved by taking into account the variation of the reaction driving force with temperature.^{3,20} In this analysis, the pre-exponential factor was assumed to be $Z^{\text{hom}} = \chi_{\text{el}} k_{\text{coll}}^{\text{hom}}$ in which χ_{el} is the transmission factor ($0 < \chi_{\text{el}} < 1$) resulting from proton tunneling through the transition-state barrier and $k_{\text{coll}}^{\text{hom}} = N_A \sigma^2 \sqrt{8\pi RT/M}$ is the collision factor for a bimolecular reaction (where σ is the sum of the molecular equivalent radii of the reactants and M is the reduced mass).

This formulation implicitly assumes that the reaction takes place only at the contact distance, σ , between the reactants. Thus, alike the electrochemical case, the treatment should be improved by taking into account that the CPET reaction may take place at various distances between the reactants (see section 4). We will see that the rate constant may then be expressed as follows:

$$k_{\text{hom}} = Z_{\text{hom}} \exp \left[-\frac{\lambda^{\text{hom}}}{4RT} \left(1 + \frac{\Delta G^0 - \Delta ZPE}{\lambda^{\text{hom}}} \right)^2 - \frac{\Delta ZPE^\ddagger}{RT} \right] \quad (3)$$



Scheme 4 Homogeneous PCET oxidation of **2** by a series of triarylamine cation radicals.

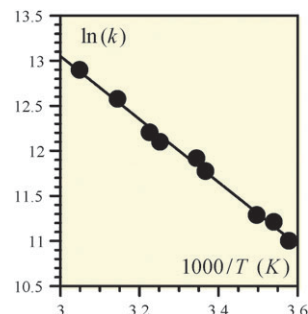


Fig. 2 Arrhenius plots for the oxidation of **2** in acetonitrile a triarylamine cation radical, from the data in ref. 5. k in M⁻¹ s⁻¹, T in K.

λ^{hom} , involves heavy-atom reorganization not only in the molecule that undergoes the CPET reaction but also in the electron-acceptor molecule. The rate constant-driving force relationship may be linearized in the same way as in ref. 3 and 20, and, taking into account that:

$$\Delta G^0 = -F(E_{A^{\bullet+}/A}^0 - E_{2^{\bullet+}/2}^0) = \Delta H^0 - T\Delta S^0$$

where $E_{A^{\bullet+}/A}^0$ is the standard potential of the electron-acceptor couple.

It becomes:

$$\ln(k_{\text{hom}}) = \ln(Z^{\text{hom}}) + \frac{\Delta S^0}{2R} - \frac{\frac{\lambda^{\text{hom}}}{4} + \frac{\Delta H^0}{2} + \Delta ZPE^\ddagger - \frac{\Delta ZPE}{2}}{RT} \quad (4)$$

The data from ref. 5 are thus fitted (Fig. 2) with eqn (4) leading to $\ln(Z^{\text{hom}}) + \frac{\Delta S^0}{2R} = 23.54$ and $\frac{\lambda^{\text{hom}}}{4} + \frac{\Delta H^0}{2} + \Delta ZPE^\ddagger - \frac{\Delta ZPE}{2} = 0.301$ eV. It follows that (with $\Delta S^0 = 0.418$ meV K⁻¹,²⁰ $\Delta H^0 = 0.103$ eV²⁰ and $\Delta ZPE^\ddagger - \frac{\Delta ZPE}{2} = -0.04$ eV³): $Z^{\text{hom}} = 1.48 \times 10^9$ M⁻¹ s⁻¹ and $\lambda^{\text{hom}} = 1.16$ eV.

3. Improved treatment of the electrochemical data

3.1 Taking into account that proton–electron transfer may take place at various distances from the electrode surface

The description of the CPET electrochemical kinetics in ref. 3 was based on the assumption that the electron transfer, concerted with proton transfer, occurs when the reactant is at a given distance from the electrode, referred to as the reaction site, usually assumed to be located at the outer Helmholtz plane. Linearization of the resulting current-potential law thus led to a Butler-Volmer law and an Arrhenius variation with temperature. The slope of the Arrhenius plot provided an estimation of the heavy-atom reorganization energy and the intercept, information about proton tunneling and its degree of adiabaticity. The H/D kinetic isotope effect is reflected in two ways in the model. One derives from the zero-point energy terms in the slope of the Arrhenius plot (see eqn (2)). The other is contained in the

pre-exponential factor and reflects proton tunneling through the transition state barrier, if any. If the CPET reaction is adiabatic, the H/D kinetic isotope effect only appears in the zero-point energy terms in the Arrhenius slope. In application of the model of ref. 3 to **1**, the pre-exponential factor was taken as:

$$Z^{\text{het}} = \chi_{\text{el}} k_{\text{coll}}^{\text{het}} \frac{\pi}{\sqrt{1 + \pi RT/\lambda^{\text{het}}}} \sqrt{\frac{RT}{4\pi\lambda^{\text{het}}}} \simeq \chi_{\text{el}} k_{\text{coll}}^{\text{het}} \pi \sqrt{\frac{RT}{4\pi\lambda^{\text{het}}}}$$

The H/D kinetic isotope effect on the pre-exponential factor on the slope was neglected, considering that the reaction was adiabatic, retaining only the zero-point energy effect.

Such a simple treatment of the effect of the degree of adiabaticity is no longer possible if one takes into consideration the possibility of electron transfer at any distance from the electrode. The following analysis of the problem starts with the establishment of a rate law that is applicable to both simple electron transfers and to CPET reactions. The two cases will be then distinguished so as to develop a strategy allowing the characterization of proton tunneling even though it cannot be expressed by the magnitude of a single parameter. This treatment will also involve consideration of all electronic states in the electrode.

The reaction rate is considered as the rate at which the decomposition of the activated complex occurs, which may be taken as equal to the frequency of vibration ν_n of the activated complex along the reaction coordinate.²¹ Then, from the activated complex theory, at a distance r from the electrode and for an electron energy \mathbf{E} , the heterogeneous rate constant $k_{\text{het}}(r, \mathbf{E})$ (s^{-1}) may be expressed as:

$$k_{\text{het}}(r, \mathbf{E}) = \nu_n \chi_{\text{el}} \kappa_n \quad (5)$$

where χ_{el} is the electronic transmission coefficient and

$$\kappa_n(\mathbf{E}) = \exp\left[-\frac{\lambda^{\text{het}}}{4RT} \left(1 + \frac{\Delta G^0 - \Delta ZPE}{\lambda^{\text{het}}}\right)^2 - \frac{\Delta ZPE^{\neq}}{RT}\right] \quad (6)$$

is the nuclear factor. ΔG^0 is the driving force of the reaction which depends on \mathbf{E} the energy of the electron in the electrode and on its value when the electrode potential is equal to the standard potential of the redox couple E^0 as well as on ϕ_S , the potential difference between the reactant site and the solution. Since the potential drop within the layer in which the rate constant has a significant value is small, the nuclear factor may be considered as independent of r . Note also that it is assumed that the coupling of electronic states at the transition state does not significantly modify the activation barrier estimated from a quadratic model. The heterogeneous rate constant at a given r distance $k_{\text{het}}(r)$ is obtained after averaging over the equilibrium electron distribution function in the metal:

$$k_{\text{het}}(r) = \frac{\int \nu_n \chi_{\text{el}} \kappa_n \rho_e \, d\mathbf{E}}{\int \rho_e \exp\left(-\frac{\mathbf{E}}{RT}\right) \, d\mathbf{E}}$$

where ρ_e is the density of the states assumed to be independent on \mathbf{E} .^{13,22}

$$\int \rho_e \exp\left(-\frac{\mathbf{E}}{RT}\right) \, d\mathbf{E} = \rho_e RT$$

Then

$$k_{\text{het}}(r) = \nu_n \int \chi_{\text{el}} \kappa_n \frac{d\mathbf{E}}{RT}$$

From eqn (6) linearized over the relatively narrow potential excursions in most electrochemical experiments, one obtains for the potential-dependent rate constant at fixed r :

$$k_{\text{het}}(r) = \nu_n \exp\left(-\frac{\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\neq} - \frac{\Delta ZPE}{2}}{RT}\right) \times \exp\left(\frac{F(E-E^0)}{2RT}\right) \times \int \chi_{\text{el}} \exp\left(-\frac{(\mathbf{E}-\mathbf{E}_F)}{2RT} \left(1 + \frac{(\mathbf{E}-\mathbf{E}_F)}{2\lambda^{\text{het}}}\right)\right) \frac{d\mathbf{E}}{RT}$$

A relationship that has the same form as the Butler-Volmer law:^{17,23}

$$k_{\text{het}}(r) = k_S^{\text{het}}(r) \exp\left[\frac{F}{2RT}(E-E^0)\right]$$

with as standard rate constant:

$$k_S^{\text{het}}(r) = \nu_n \exp\left(-\frac{\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\neq} - \frac{\Delta ZPE}{2}}{RT}\right) \times \int \chi_{\text{el}} \exp\left(-\frac{(\mathbf{E}-\mathbf{E}_F)}{2RT} \left(1 + \frac{(\mathbf{E}-\mathbf{E}_F)}{2\lambda^{\text{het}}}\right)\right) \frac{d\mathbf{E}}{RT}$$

It is assumed that the electronic transmission coefficient χ_{el} at a given energy is determined by the product of two factors: a probability χ_e independent from \mathbf{E} and a Fermi distribution function $f(\mathbf{E})$, leading to:

$$\int \chi_{\text{el}} \exp\left(-\frac{\zeta}{2}\right) \exp\left(-\frac{RT\zeta^2}{4\lambda^{\text{het}}}\right) \, d\zeta = \chi_e \int f(\zeta) \exp\left(-\frac{\zeta}{2}\right) \exp\left(-\frac{RT\zeta^2}{4\lambda^{\text{het}}}\right) \, d\zeta = \chi_e \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}}$$

and thus:

$$k_S^{\text{het}}(r) = \nu_n \chi_e \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} \exp\left(-\frac{\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\neq} - \frac{\Delta ZPE}{2}}{RT}\right)$$

The next step is the evaluation of the integral $\int_{r_0}^{\infty} k_S^{\text{het}}(r) c(r) \, dr$ where r_0 is the least distance of approach of the substrate and $c(r)$ its concentration at a given distance, r . Because the transmission coefficient $\chi_{\text{el}}(r)$ diminishes quite sharply with r (see below), whereas $c(r)$ changes smoothly, $c(r)$ can be regarded as approximately constant in the region of interest. The applicability of the Butler-Volmer law (eqn (1))

ensues as well as the expression of the standard rate constant, obtained from $k_S^{\text{het}} = \int_{r_0}^{\infty} k_S^{\text{het}}(r) dr$ as:

$$k_S^{\text{het}} = \nu_n \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} I_{\text{el}} \exp\left(-\frac{\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\ddagger} - \frac{\Delta ZPE}{2}}{RT}\right)$$

where $I_{\text{el}} = \int_{r_0}^{\infty} \chi_e(r) dr$. It is then confirmed that the standard rate constant does obey eqn (2):

$$k_S^{\text{het}} = Z^{\text{het}} \exp\left(-\frac{\frac{\lambda^{\text{het}}}{4} + \frac{F}{2}\phi_S + \Delta ZPE^{\ddagger} - \frac{\Delta ZPE}{2}}{RT}\right)$$

with:

$$Z^{\text{het}} = \nu_n \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} I_{\text{el}}$$

The final step of the analysis consists in looking for an expression of $\chi_e(r)$. A rigorous theoretical treatment of the strong electronic coupling limit between the reactant and the electrode is complicated^{24,25} and a description of the whole range of electronic coupling is even more problematic.²⁶ We thus use as a starting point a phenomenological approach using a Landau–Zener formulation allowing an interpolation between adiabatic and non-adiabatic behaviors²⁷ and an exponential distance dependence of the coupling between electronic states at the transition state, $C(r) = C_0 \exp\left(-\frac{\beta(r-r_0)}{2}\right)$ where C_0 is the coupling constant when $r = r_0$ leading to:^{28,29}

$$Z^{\text{het}} = \frac{\nu_n}{\beta} \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} \int_0^{\infty} \frac{2 - 2 \exp\left(-\frac{\pi^2 C_0^2 \exp(-x)}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}}\right)}{2 - \exp\left(-\frac{\pi^2 C_0^2 \exp(-x)}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}}\right)} dx$$

which can be approximated by:¹⁷

$$Z^{\text{het}} = \frac{\nu_n}{\beta} \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} \ln\left(1 + \frac{2\pi^2 C_0^2}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}}\right) \quad (7)$$

C_0^2 , the coupling constant, is averaged over all the wave vectors contributing to a given energy E , and the resulting value is assumed to be independent on the value of this energy,^{22,30} thus leading to the assumption made above that $\chi_e(r)$ is independent from E .

It thus appears that taking into account the fact that the electron transfer reaction may take place at various distances from the electrode surface implies that the pre-exponential factor continuously increases with C_0 (Fig. 3) without reaching a limiting value. There are nevertheless two distinct domains of variation. At low values of C_0 , the pre-exponential factor is proportional to C_0^2 whereas it varies smoothly with C_0 for higher values. The first region may be referred to as non-adiabatic while the other may be referred to as adiabatic. However, the notion of adiabaticity itself is blurred. Indeed, even though the transfer may be adiabatic at short distances, it

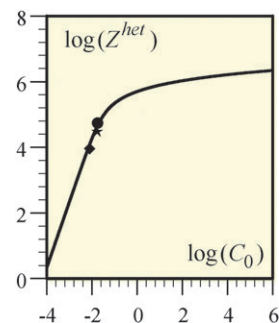


Fig. 3 Variation of the pre-exponential factor with the coupling constant at the distance of closest approach to the electrode. $\nu_n = 2 \times 10^{12} \text{ s}^{-1}$, $\beta = 10^8 \text{ cm}^{-1}$, $\lambda^{\text{het}} = 1.4 \text{ eV}$, $T = 298 \text{ K}$. Dot: Outersphere electron transfer (see text). Star: CPET with hydrogenated **1**. Diamond: CPET with deuterated **1**. Z^{het} in cm s^{-1} , C_0 in eV.

always ended to be non-adiabatic at long distances. Under these conditions, the best strategy to characterize the effect of proton transfer on the degree of adiabaticity, using the pre-exponential factor as an observable, is to compare the pre-exponential factor of the CPET reaction obtained from the corresponding Arrhenius plot of interest to the pre-exponential factor of a simple outersphere electron transfer involving a comparable substrate under similar experimental conditions. Section 3.2. is devoted to the analysis of such a reference outersphere electron transfer.

3.2 An example of application to a simple outersphere electron transfer

Experimental data related to the temperature dependence of outersphere electron transfer rate constant, with free diffusing reactants, are not very numerous, concerning transition metal complexes^{31–35} or organic molecules.^{36–41} We consider here the experimental data gathered in ref. 38 for the reduction of nitromesitylene at a mercury electrode in propylene carbonate in presence of various tetraalkylammonium cations salts. Analysis of the Arrhenius plots given in Fig. 5 of ref. 38 with the rate constant expression $k_S^{\text{het}} = Z^{\text{het}} \exp(-\lambda_{\text{ap}}^{\text{het}}/4RT)$ leads to the estimation of the pre-exponential factor Z^{het} (Table 1) as a function of the tetraalkylammonium cation and of the apparent reorganization energy $\lambda_{\text{ap}}^{\text{het}} = 1.2 \text{ eV}$.

Fig. 4 shows that the pre-exponential factor Z^{het} is correlated with the radius of tetraalkylammonium cations, r_+ , in agreement with eqn (7), considering that the distance of minimal approach is $r_0 = r_+$, and according to:

$$C_0 = C_{00} \exp(-ar_+). \quad (8)$$

Table 1 Data

Cation	$Z^{\text{het}}/\text{cm s}^{-1}$	Radius, $r_+/\text{\AA}^{42}$
Tetraethylammonium	28 888	3.37
Tetrapropylammonium	16 512	3.72
Tetrabutylammonium	8103	4.13
Tetrahexylammonium	4183	4.69
Tetraoctylammonium	2930	5.03

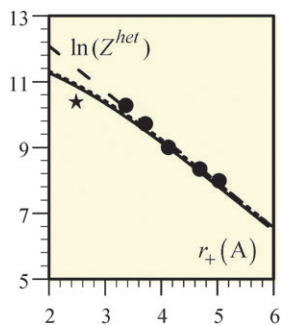


Fig. 4 Variation of pre-exponential factor with the cation radius. Dots: Reduction of nitromesitylene at a mercury electrode in propylene carbonate in presence of various tetraalkylammonium cations. Star: CPET with **1**. Dashed line: non-adiabatic behavior. Dotted line: working curve for outersphere electron transfer from reduction of nitromesitylene data. Full line: working curve for outersphere electron transfer with $\lambda^{\text{het}} = 1.46$ eV. Z^{het} in cm s^{-1} .

Indeed, for large enough values of r_+ , eqn (7) becomes:

$$\ln(Z^{\text{het}}) \simeq \ln \left[\left(\frac{\nu_n}{\beta} \pi \right) \left(\frac{2\pi^2 C_{00}^2}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}} \right) \right] - 2ar_+$$

showing a linear correlation between $\ln(Z^{\text{het}})$ and r_+ (dashed line in Fig. 4), which leads to $a = 0.69 \text{ \AA}^{-1}$ and

$$\left(\frac{\nu_n}{\beta} \pi \right) \left(\frac{2\pi^2 C_{00}^2}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}} \right) = 2.85 \times 10^6 \text{ cm s}^{-1}.$$

It is also noteworthy that the same treatment of the data obtained for the reduction of C_{60} in acetonitrile with tetra-butylammonium as electrolyte cation⁴⁰ leads to $Z^{\text{het}} = 7350 \text{ cm s}^{-1}$ ($\lambda_{\text{ap}}^{\text{het}} = 1.05$ eV), thus falling approximately on the same correlation line. This correlation may thus be used as working curve for estimating outersphere electron transfer pre-exponential factors. However, as shown above, all experimental data from ref. 38 fall in the non-adiabatic region (dashed line in Fig. 4). In order to obtain the working curve corresponding to the adiabatic region, corresponding to short r_+ values, it is necessary to evaluate separately the values of

the parameters $\left(\frac{\nu_n}{\beta} \pi \right)$ and $\left(\frac{2\pi^2 C_{00}^2}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}} \right)$. Rather than

making a guess on one or the other parameters, we make an *a fortiori* assumption assuming that the transition from non-adiabatic and adiabatic regions begins at $r_+ \simeq 3.5 \text{ \AA}$ which corresponds to the shorter approach distance thus leading to a possible overestimation of the adiabatic regime. Under this constraint, both parameters can be evaluated as

$$\left(\frac{\nu_n}{\beta} \pi \right) = 6 \times 10^4 \text{ cm s}^{-1} \text{ and } \left(\frac{2\pi^2 C_{00}^2}{h\nu_n \sqrt{4\pi RT \lambda^{\text{het}}}} \right) = 47.$$

The working curve for outersphere electron transfer pre-exponential factor is then obtained for the whole range of r_+ values (dotted line in Fig. 4). Note that the use of this working curve for others systems only requires the modification of both parameters by correction of the reorganization energy value. Note also that if we consider $\beta = 10^8 \text{ cm}^{-1}$ and $\lambda^{\text{het}} = 1.2$ eV, we obtain $\nu_n = 2 \times 10^{12} \text{ s}^{-1}$, slightly smaller

than $k_B T/h$ and a value of $C_{00} = 0.115$ eV that would definitively correspond to an adiabatic behavior.

3.3 Application to the oxidation of **1**

Eqn (7) may now be applied to the CPET oxidation of **1**, for which $Z^{\text{het}} = Z^{\text{het,CPET}} = 34\,580 \text{ cm s}^{-1}$ (from the intercept of the Arrhenius plot in Fig. 1). In order to evaluate the impact of proton transfer on the kinetics of the CPET reaction, we compare this value to the pre-exponential factor, noted $Z^{\text{het,ET}}$, for a simple outersphere electron transfer occurring in the same conditions. In this purpose, the working curve derived from the empirical relationship (8) may be applied in the present case, transposing reduction into oxidation and electrolyte cation into electrolyte anion. The minimal approach distance is then the radius of the PF_6^- anion (2.46 \AA^{42}). The working curve is then recalculated so as to take into account $\lambda^{\text{het}} = 1.5$ eV (full line in Fig. 4). At the minimal approach distance 2.46 \AA we obtain $Z^{\text{het,ET}} = 5.4 \times 10^4 \text{ cm s}^{-1}$. It is thus found that $Z^{\text{het,CPET}}/Z^{\text{het,ET}} = 0.7$, noting that this value is certainly imprecise owing to the approximations made in the working curve building procedure. It nevertheless follows that the electrochemical oxidation of **1** can be characterized as being non-adiabatic thus modifying the conclusion reached in ref. 3. The non-adiabatic character of the reaction falls in line with the experimental kinetic isotope effect $Z^{\text{het,CPET}}/Z_D^{\text{het,CPET}} = 3.5$. From the variation of the pre-exponential factor with the coupling constant for a given set of parameters ($\beta = 10^8 \text{ cm}^{-1}$, $\lambda^{\text{het}} = 1.4$ eV, $T = 298$ K) shown in Fig. 3, it can be seen that the outersphere electron transfer and the CPET fall in the non-adiabatic region. This semi-quantitative representation shows that observation of a KIE on the pre-exponential factor is reasonable in spite of the uncertainties on the parameter values.

Theoretical modeling of $Z^{\text{het,CPET}}$ according to eqn (7) may be done following the same procedure as depicted in ref. 3 to evaluate the CPET coupling constant and taking into account the effect of the proton donor-acceptor distance Q vibration. The contribution of each distance Q to proton tunnelling is obtained by weighting the pre-exponential factor by the Boltzmann probability $P(Q)$ that the donor and acceptor atoms be at a distance Q from one another:

$$Z^{\text{het}} = \int_0^\infty \frac{\nu_n}{\beta} \frac{\pi}{\sqrt{1 + \frac{\pi RT}{\lambda^{\text{het}}}}} \ln \left(1 + \frac{2\pi^2 C_{00}^2(Q)}{h\nu_n \sqrt{4\pi \lambda^{\text{het}} RT}} \right) P(Q) dQ \quad (9)$$

with

$$P(Q) = \sqrt{\frac{f_Q}{2\pi RT}} \exp \left(-\frac{f_Q(Q - Q_{\text{eq}})^2}{2RT} \right), \quad f_Q = 4\pi^2 \nu_Q^2 m_Q$$

(where ν_Q is frequency and m_Q is reduced mass). The pre-exponential factor is then estimated by numerical evaluation of eqn (9), leading to the definition of an effective coupling

constant C_0^{eff} (for details see ESI†):

$$\ln \left(1 + \frac{2\pi^2 (C_0^{\text{eff}})^2}{h\nu_n \sqrt{4\pi\lambda^{\text{het}} RT}} \right) = \int_0^\infty \ln \left(1 + \frac{2\pi^2 C_0^2(Q)}{h\nu_n \sqrt{4\pi\lambda^{\text{het}} RT}} \right) P(Q) dQ.$$

It turns out that $C_0^{\text{eff}} = 1.25 \times 10^{-3}$ eV, leading (with the same parameters as in the captions of Fig. 3) to $Z^{\text{het}} = 100 \text{ cm s}^{-1}$, which is well below the value that can be estimated from the experimental value, $34\,580 \text{ cm s}^{-1}$. This difference has been deemed to derive from the effect of the strong electric field within which the electrochemical reaction takes place under the assumption that the electron transfer coupling constant is large enough to assure adiabaticity but small enough not to affect the height of the proton barrier significantly.³

4. Improved treatment of the homogeneous data

4.1 Taking into account that proton–electron transfer may take place at various distances between the reactants

That electron transfer may occur over a range of separation distances has long been considered for outersphere reactions.⁴³ The rate constant is obtained by integration over the equilibrium distribution of separation distances, weighted by its own characteristic rate constant $k_{el}(r)$:

$$k_{\text{hom}} = \int_\sigma^\infty K_A(r) k_{el}(r) dr$$

where

$$K_A(r) = \frac{4\pi N_A r^2 dr}{1000} \exp\left(-\frac{w(r)}{RT}\right)$$

is the equilibrium constant for the formation of the reactant pairs separated by a distance between r and $r + dr$ and $w(r)$ is the work required to bring the reactant at a separation distance r (usually assumed to be a purely electrostatic term). Similarly to the heterogeneous case, $k_{el}(r) = \nu_n \chi_{el} \kappa_n$ where $\chi_{el}(r)$ is the electronic transmission coefficient and

$$\kappa_n = \exp \left[-\frac{\lambda^{\text{hom}}}{4RT} \left(1 + \frac{\Delta G^0 - \Delta ZPE}{\lambda^{\text{hom}}} \right)^2 - \frac{\Delta ZPE^\ddagger}{RT} \right]$$

is the nuclear factor. ΔG^0 is the driving force of the reaction. According to the same description of the electronic transmission coefficient as in the heterogeneous case, one obtains:

$$k_{\text{hom}} = Z^{\text{hom}} \exp \left[-\frac{\lambda^{\text{hom}}}{4RT} \left(1 + \frac{\Delta G^0 - \Delta ZPE}{\lambda^{\text{hom}}} \right)^2 - \frac{\Delta ZPE^\ddagger}{RT} \right]$$

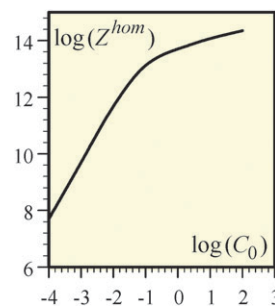


Fig. 5 Variation of the pre-exponential factor with the coupling constant at the closest distance between reactants. $\nu_n = k_B T/h$, $\beta = 10^8 \text{ cm}^{-1}$, $\lambda^{\text{hom}} = 1.2 \text{ eV}$, $T = 298 \text{ K}$ and $\sigma = 8 \text{ \AA}$. Z^{hom} in $\text{M}^{-1} \text{ s}^{-1}$, C_0 in eV.

with:

$$Z^{\text{hom}} = \int_\sigma^\infty \nu_n \frac{4\pi N_A r^2}{1000} \times \exp\left(-\frac{w(r)}{RT}\right) \frac{2 - 2 \exp\left(-\frac{\pi^2 C_0^2 \exp[-\beta(r-\sigma)]}{h\nu_n \sqrt{4\pi RT} \lambda^{\text{hom}}}\right)}{2 - \exp\left(-\frac{\pi^2 C_0^2 \exp[-\beta(r-\sigma)]}{h\nu_n \sqrt{4\pi RT} \lambda^{\text{hom}}}\right)} dr \quad (10)$$

σ is the distance of minimal approach of the reactants. To simplify presentation we treat the case where $w(r) = 0$ (meaning that at least one reaction is uncharged). In this case too, this formulation shows that taking into account the fact that the electron transfer reaction may take place at various distances between reactants leads to a pre-exponential factor that continuously increases with the coupling constant, C_0 (Fig. 5). The same conclusion as in the heterogeneous case ensues: estimation of the impact of the proton transfer concerted with electron transfer in CPET reactions based on the determination of the pre-exponential factor deriving from an Arrhenius plot requires a comparison with the pre-exponential factor corresponding to a simple outersphere electron transfer taking place in similar conditions as the CPET of interest.

4.2 Application to the oxidation of 2

Eqn (10) may now be applied to analyze the CPET oxidation of **2** depicted in Scheme 4, which led to $Z^{\text{hom}} = 1.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (from the intercept of the Arrhenius plot in Fig. 2). Taking $\nu_n = k_B T/h$, $\beta = 10^8 \text{ cm}^{-1}$, $\sigma = 8 \text{ \AA}$, and knowing from the slope that $\lambda^{\text{hom}} = 1.16 \text{ eV}$, application of eqn (10) leads to $C_0^{\text{CPET}} = 5.5 \times 10^{-4} \text{ eV}$ —a small value that points to a non-adiabatic regime. In this case there is no obvious comparison with a simple outersphere electron transfer, which would be the best way to treat the problem.

We may however theoretically estimate the coupling constant, keeping the same parameters as used above, using the procedure depicted in ref. 3. The experimental value is small enough for the non-adiabatic limit to be reached, leading to a linear variation of Z^{hom} with C_0^2 . The effect of proton donor–acceptor distance Q vibration on the CPET coupling constant may thus be introduced by weighting the pre-exponential

factor by the Boltzmann probability $P(Q)$ that the donor and acceptor atoms be at a distance Q from one another:

$$Z^{\text{hom}} = \left(\frac{1 + (1 + \beta\sigma)^2}{(\beta\sigma)^2} \right) \frac{4\pi N_A \sigma^2}{1000 \beta} \frac{\pi^2}{h\sqrt{4\pi RT}\lambda^{\text{hom}}} \\ \times \int_0^\infty C_0^2(Q)P(Q) dQ$$

The effective coupling constant C_0^{eff} is then given by:

$$C_0^{\text{eff}^2} = \int_0^\infty C_0^2(Q)P(Q) dQ \quad (7)$$

leading to $C_0^{\text{eff}} = 1.3 \times 10^{-3}$ eV (parameters for numerical calculation are given in the ESI†), a value of the same order as the experimental value, $C_0^{\text{CPET}} = 5.5 \times 10^{-4}$ eV. It follows that, the homogeneous CPET oxidation of **2** is non-adiabatic as already concluded from our previous analysis, in contrast with the mildly non-adiabatic character of the heterogeneous oxidation of **1**.³ This difference in behavior may be assigned to an electric field effect in the latter case.

Conclusions

Reorganization energies are derived from the slopes of the Arrhenius plots obtained from the temperature dependence of the oxidation rate constant in the electrochemical and homogeneous cases. The intercept of the Arrhenius plots potentially contain information on the role of proton transfer in the dynamics of the concerted proton–electron transfer reaction (CPET). Previous analyses of the problem were based on equating the pre-exponential factor in the absence of barrier for proton-tunneling with the collision frequency. Taking into account that the reaction may take place at various distances from the electrode surface increases the value of this limiting pre-exponential factor and thus modifies the estimation of impact of proton transfer on the kinetics of the CPET reaction. The best strategy in this respect is to compare the experimental CPET pre-exponential factor to the pre-exponential factors obtained with simple outersphere electron transfer reaction. The main conclusion of the present study is that the electrochemical oxidation of **1** is mildly non-adiabatic in line with the observation of a KIE on the pre-exponential factor whereas it is confirmed that the homogeneous oxidation of **2** is clearly non-adiabatic.

Glossary

a	decay constant for coupling constant with supporting electrolyte ion radius
$c(r)$	substrate concentration at a r distance from the electrode
$C(r)$	coupling constant at a r distance between the electrode and the substrate (for an heterogeneous reaction) or between reactants (for an homogeneous reaction)
C_0	coupling constant at a r_0 distance between the electrode and the substrate (for an heterogeneous reaction) or at σ distance between reactants (for an homogeneous reaction)

C_0^{CPET}	C_0 for a CPET reaction
C_0^{eff}	effective C_0 taking into account the effect of modulation of the proton donor–acceptor distance
C_{00}	coupling constant extrapolated at zero distance between electrode and reactant
E	electron energy level in the electrode
E	electrode potential
E^0	standard potential
F	Faraday constant
$f(\mathbf{E})$	Fermi–Dirac distribution
f_Q	force constant for proton donor–acceptor frequency
h	Planck constant
i	current
I_{el}	integral resulting from integration of the electronic transmission coefficient over distances
$K_A(r)$	equilibrium constant for the reaction of the reactant pair in homogeneous bimolecular reaction
k_B	Boltzmann constant
$k_{\text{coll}}^{\text{het}}$	heterogeneous collision frequency
k_{het}	heterogeneous rate constant
$k_{\text{het}}(r, \mathbf{E})$	heterogeneous rate constant at a given r distance and \mathbf{E} electron energy
k_{∞}^{het}	heterogeneous rate constant reached for an adiabatic reaction in the absence of heavy atoms reorganization
k_S^{het}	standard rate constant for heterogeneous reaction
$k_S^{\text{het,ap}}$	apparent standard rate constant for heterogeneous reaction
$k_{\text{coll}}^{\text{hom}}$	bimolecular homogeneous collision frequency
k_{hom}	homogeneous rate constant
M	mass of the substrate in heterogeneous reaction
m_Q	reduced mass of the proton donor and acceptor sites
N_A	Avogadro's number
$P(Q)$	Boltzmann probability that the proton donor and acceptor be at a distance Q from one another
Q	proton donor and acceptor separation distance
R	gas constant
r	distance between the electrode surface and redox substrate
r_0	smallest distance between the electrode surface and redox substrate
r_+	cation radius of the supporting electrolyte
S	electrode surface area
T	temperature
$w(r)$	work required to bring reactants at a separation distance r
Z^{het}	heterogeneous pre-exponential factor
$Z^{\text{het,ET}}$	heterogeneous pre-exponential factor for a simple outersphere electron transfer
$Z^{\text{het,CPET}}$	heterogeneous pre-exponential factor for CPET
$Z_D^{\text{het,CPET}}$	heterogeneous pre-exponential factor for CPET with deuterated compound
Z^{hom}	homogeneous pre-exponential factor

α	transfer coefficient
β	decay constant for coupling constant with r
λ_{el}	electronic transmission coefficient
λ_e	averaged electronic transmission coefficient
ΔG^\ddagger	standard free enthalpy of activation
ΔG^0	standard free enthalpy of reaction
ΔH^0	standard enthalpy of reaction
ΔS^0	standard entropy of reaction
ΔZPE	difference of zero point energy between product state and reactant state
ΔZPE^\ddagger	difference of zero point energy between transition state and reactant state
ϕ_S	potential difference between reaction site and bulk
κ_n	nuclear factor
λ^{het}	heterogeneous reorganization energy
λ_{ap}^{het}	apparent heterogeneous reorganization energy
λ^{hom}	homogeneous reorganization energy
ν_n	effective nuclear vibration frequency
ν_Q	nuclear vibration frequency associated to proton donor–acceptor vibration
ρ_{el}	density of states per eV in an electrode
σ	smallest center to center donor–acceptor distance for an homogeneous bimolecular reaction

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