Adiabatic and Non-Adiabatic Concerted Proton-Electron Transfers. Temperature Effects in the Oxidation of Intramolecularly Hydrogen-Bonded Phenols

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1. Voltammograms at all investigated temperatures

Fig. 1S. Cyclic voltammetry of **1** (2.5 mM) at a glassy carbon electrode in acetonitrile + 0.1 M *n*-NBu₄PF₆. (top); in acetonitrile + 0.1 M *n*-NBu₄PF₆. + 2% CD₃OD (bottom). Scan rate: 0.5 V/s. Thin lines: experiments; bold line: simulations (see text).

2. Expression of the rate constant in the non-adiabatic limit

2.1. Averaged rate constant

$$k(E) \approx Z_{el} \langle \chi \rangle \exp \left[-\frac{\lambda}{4RT} \left(1 - \frac{F(E - E^0)}{\lambda} \right)^2 \right]$$

$$\langle \chi \rangle = \int_{-\infty}^{+\infty} \chi(Q) P(Q) dQ$$

where $P(Q)$ is the normalized Boltzmann distribution function for a classical harmonic oscillator:

$$P(Q) = \sqrt{\frac{f_Q}{2\pi RT}} \exp \left(-\frac{f_Q(Q - Q_{eq})^2}{2RT} \right)$$

In the non-adiabatic limit:

$$\chi = 2p = 2(\pi / RT)^{3/2} C^2 / \sqrt{\lambda}$$

thus:

$$\langle \chi \rangle = 2 \sqrt{\frac{f_Q}{2\pi RT}} \int_{-\infty}^{+\infty} \left(\frac{\pi}{RT} \right)^{3/2} \frac{C^2}{\sqrt{\lambda}} \exp \left(-\frac{f_Q (Q - Q_{eq})^2}{2RT} \right) dQ$$

We consider

$$C(Q) = C_{eq} \exp \left[-\beta (Q - Q_{eq}) \right]$$

This is a reasonable approximation over a wide range of Q values (figure 2S).

Fig 2S. $\ln(C)$ as a function of Q coordinate in the isosceles triangular proton potential model (see below)

Then using $\int_{-\infty}^{+\infty} \exp(-u^2) du = \sqrt{\pi}$,

$$\langle \chi \rangle = \frac{2\pi}{RT} \left(\frac{\pi}{RT\lambda} \right)^{1/2} C_{eq}^2 \exp \left(\frac{2\beta^2 RT}{f_Q} \right)$$

Finally,

$$k(E) = Z_{el} \frac{2\pi}{RT} \left(\frac{\pi}{RT\lambda} \right)^{1/2} C_{eq}^2 \exp \left(\frac{2\beta^2 RT}{f_Q} \right) \exp \left[-\frac{\lambda}{4RT} \left(1 - \frac{F(E - E^0)}{\lambda} \right)^2 - \frac{\Delta ZPE}{RT} \right]$$

2.2. Dynamical rate constant

In the non-adiabatic limit, the rate constant can be expressed as an integral of the time-dependent probability flux correlation function:^{1S}

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} \frac{1}{\hbar} \int_{-\infty}^{+\infty} j(t) dt$$

If we again consider the following expression for the coupling constant

$$C(Q) = C_{eq} \exp \left[-\beta (Q - Q_{eq}) \right]$$

and assuming that the equilibrium Q distance is identical for reactant and product :^{1S, 2S}

$$j(t) = C_{eq}^2 \exp \left[\frac{i}{\hbar} \langle \varepsilon \rangle t \right] \exp \left[\beta^2 [C_Q(0) + C_Q(t)] \right] \exp \left[-\frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} C_\varepsilon(\tau_1 - \tau_2) d\tau_2 \right]$$

where $C_Q(t)$ and $C_\varepsilon(t)$ are the time correlation function for the Q coordinate and the solvent coordinate respectively; $\langle \varepsilon \rangle$ is the averaged (on the reactant surface) energy gap between the reactant and product states.

Approximations :

(i) for an undamped classical mechanical oscillator :^{1S-3S}

$$C_Q(t) = \frac{RT}{m\omega_Q^2} \cos(\omega_Q t)$$

(ii) the coupling between the Q motion and the solvent coordinate is neglected. Moreover, we consider that the Q -coordinate time correlation function $C_Q(t)$ is approximately constant on the time scale of the probability flux correlation function decay and therefore equal to its initial value $C_Q(0) = \langle \delta Q^2 \rangle$ (i.e. the variance of the Q -coordinate):^{4S}

$$C_Q(t) \approx C_Q(0) = \frac{RT}{m\omega^2}$$

then :

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} \frac{1}{\hbar} C_{eq}^2 \exp \left[\frac{2RT\beta^2}{m\omega_Q^2} \right] \int_{-\infty}^{+\infty} \exp \left[\frac{i}{\hbar} \langle \varepsilon \rangle t \right] \exp \left[-\frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} C_{\varepsilon}(\tau_1 - \tau_2) d\tau_2 \right] dt$$

(iii) linear response approximation ^{3S, 4Sa}

$$\lambda = \frac{\langle \delta \varepsilon^2 \rangle}{2RT} \text{ and } \langle \varepsilon \rangle = \Delta G^0 + \lambda$$

(iv) short time approximation: ^{3S, 4Sa}

$$\exp \left[-\frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} C_{\varepsilon}(\tau_1 - \tau_2) d\tau_2 \right] = \exp \left[-\frac{C_{\varepsilon}(0)t^2}{2\hbar^2} \right] = \exp \left[-\frac{\lambda RT}{\hbar^2} t^2 \right]$$

thus :

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} \frac{1}{\hbar} C_{eq}^2 \exp \left[\frac{2RT\beta^2}{m\omega_Q^2} \right] \int_{-\infty}^{+\infty} \exp \left[\frac{i}{\hbar} (\Delta G^0 + \lambda) t \right] \exp \left[-\frac{\lambda RT}{\hbar^2} t^2 \right] dt$$

taking $\omega_Q t = \tau$ then

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} \frac{1}{\hbar \omega_Q} C_{eq}^2 \exp \left[\frac{2RT\beta^2}{m\omega_Q^2} \right] \int_{-\infty}^{+\infty} \exp \left[i \left(\frac{\Delta G^0 + \lambda}{\hbar \omega_Q} \right) \tau \right] \exp \left[-\frac{1}{2} \left(\frac{2\lambda RT}{\hbar^2 \omega_Q^2} \right) \tau^2 \right] d\tau$$

i.e.

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} \frac{2}{\hbar \omega_Q} C_{eq}^2 \exp \left[\frac{2RT\beta^2}{m\omega_Q^2} \right] \hat{j} \text{ avec } \hat{j} = \frac{1}{2} \int_{-\infty}^{+\infty} \exp[i r \tau] \exp \left[-\frac{RT}{\hbar \omega_Q} s \tau^2 \right] d\tau$$

with

$$r = \frac{\Delta G^0 + \lambda}{\hbar \omega_Q} \text{ and } s = \frac{\lambda}{\hbar \omega_Q}$$

using stationary phase method : ^{2S, 5S}

$$\hat{j} = \frac{1}{2} \int_{-\infty}^{+\infty} \exp[\psi(\tau)] d\tau \approx \frac{1}{2} \left(\frac{2\pi}{|\psi''(\tau_s)|} \right)^{1/2} \exp[\psi(\tau_s)]$$

with $\psi(\tau) = i r \tau - \frac{RT}{\hbar \omega_Q} s \tau^2$ and τ_s defined by

$$-i \psi'(\tau_s) = r + 2i \frac{RT}{\hbar \omega_Q} s \tau_s = 0 \text{ i.e. } \tau_s = i \frac{\hbar \omega_Q}{2RT} \frac{r}{s}$$

then :

$$\psi(\tau_s) = -\frac{\hbar \omega_Q}{2RT} \frac{r^2}{s} + \frac{RT}{\hbar \omega_Q} \left(\frac{\hbar \omega_Q}{2RT} \right)^2 \frac{r^2}{s} = -\frac{\hbar \omega_Q}{4RT} \frac{(\Delta G^0 + \lambda)^2}{\lambda \hbar \omega_Q} = -\frac{\lambda}{4RT} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2$$

$$\frac{1}{2} \left(\frac{2\pi}{|\psi''(\tau_s)|} \right)^{1/2} = \frac{\hbar \omega_Q}{2} \left(\frac{\pi}{RT \lambda} \right)^{1/2}$$

thus leading to:

$$k_{dyn} = Z_{el} \frac{2\pi}{RT} C_{eq}^2 \exp \left[\frac{2RT\beta^2}{m\omega_Q^2} \right] \left(\frac{\pi}{RT \lambda} \right)^{1/2} \exp \left[-\frac{\lambda}{4RT} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \right]$$

This expression is exactly the same as the one derived above from classical averaging.

3. Linearization of the electrochemical rate law

The expression of the vibrational state(μ)-to-state(ν) rate constant, $k_{j,\mu\nu}$, is: (j indicates the electrode electronics state)

$$k_{j,\mu\nu} = Z_{el} \chi_{\mu\nu} \exp \left(-\frac{\Delta G_{j,\mu\nu}^\ddagger}{RT} \right)$$

with the transmission factor $\chi_{\mu\nu}$ being:

$$\chi_{\mu\nu} \approx \frac{2p_{\mu\nu}}{1 + p_{\mu\nu}}$$

and the transmission probability $p_{\mu\nu}$:

$$p_{\mu\nu} = 1 - \exp\left(-\frac{\pi C_{\mu\nu}^2}{RT} \sqrt{\frac{\pi}{RT\lambda}}\right)$$

Z_{el} is the electrochemical collision factor:

$$Z_{el} = \sqrt{\frac{RT}{2\pi M}}$$

M is the molar mass, $C_{\mu\nu}$ is the coupling between electronically diabatic states and λ is the reorganization energy. We consider the case of an oxidation and the transfer of only one electron ($R = P + e$):

$\Delta G_{j,\mu\nu}^\ddagger$, the activation free energy, is given by:

$$\Delta G_{j,\mu\nu}^\ddagger = w_{R,0} + \mu\hbar\omega_R + \frac{1}{4\lambda} \left(\lambda - (-\mathbf{E}_j + \mathbf{E}_{\mu\nu}^0 - w_{P,0} + w_{R,0}) \right)^2 + (2\mu + 1)\Delta ZPE$$

$\mathbf{E}_j$ is the energy of the electron in the metal and $\mathbf{E}_{\mu\nu}^0 = \mathbf{E}_{00}^0 + \mu\hbar\omega_R - \nu\hbar\omega_P$ its value when the electrode potential is equal to the standard potential of the redox couple, $\mathbf{E}_{\mu\nu}^0$ with the proton vibration being in the reactant μ^{th} state and product ν^{th} states. ΔZPE is the variation of the zero point energy between the reactant and the transition state. We assume here that this difference is independent from the driving force.

In a cyclic voltammetry experiment where the extent of potential investigated is limited, the quadratic relationship can be linearized around the half-wave potential $E_{1/2}$.

$$\Delta G_{j,\mu\nu}^\ddagger = w_{R,\mu} + \frac{1}{4\lambda} \left(\lambda - (-\mathbf{E}_j + \mathbf{E}_{00}^0 - w_{P,\nu} + w_{R,\mu}) \right)^2 + (2\mu + 1)\Delta ZPE$$

with

$$w_{R,\mu} = w_{R,0} + \mu\hbar\omega_R$$

$$w_{P,\nu} = w_{P,0} + \nu\hbar\omega_P$$

Thus,

$$\Delta G_{j,\mu\nu}^\ddagger = w_{R,\mu} + \frac{1}{4\lambda} \left(\lambda - (-\mathbf{E}_j + \mathbf{E}_{00}^0 - w_{P,\nu} + w_{R,\mu}) \right)^2 + (2\mu + 1)\Delta ZPE$$

$$\mathbf{E}_F = \mathbf{E}_{1/2} + \Delta E$$

where $\mathbf{E}_{1/2}$ is the energy of the electron in the metal when the electrode potential is equal to $E_{1/2}$.

$$\begin{aligned} & \frac{1}{4\lambda} \left(\lambda + \mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + \Delta E + w_{P,\nu} - w_{R,\mu} \right)^2 = \\ & \frac{1}{4\lambda} \left(\lambda + \mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu} \right)^2 \left(1 + \frac{\Delta E}{\lambda + \mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu}} \right)^2 \end{aligned}$$

The second term may be linearized,

$$\approx \frac{1}{4\lambda} \left(\lambda + \mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu} \right)^2 + \frac{1}{2} \left(1 + \frac{\mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu}}{\lambda} \right) \Delta E$$

The following approximation is then made:

$$\frac{1}{2} \left(1 + \frac{\mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\mu} - w_{R,\nu}}{\lambda} \right) \approx \alpha_{\mu\nu}$$

in this approximation, it is considered that α does not depend on j (electronic state in the electrode). This is obviously not correct but, when all electronic states are considered only those with $\mathbf{E}_j$ close to $\mathbf{E}_F$ will have a significant weight.

Then:

$$\exp\left(-\frac{\Delta G_{j,\mu\nu}^\ddagger}{RT}\right) \approx \exp\left[-\frac{w_{R,\mu}}{RT}\right] \exp\left[-\frac{1}{4\lambda RT} \left(\lambda + \mathbf{E}_j - \mathbf{E}_F + \mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu} \right)^2\right] \exp\left(\frac{-\alpha\Delta E}{RT}\right) \exp\left(\frac{-(2\mu + 1)\Delta ZPE}{RT}\right)$$

So far, only one electronic state has been considered for the electron. However all electrode electronic states in the electrode have to be taken into account. Consequently, the vibrational state-to-state rate constant $k_{\mu\nu}$ is obtained after multiplication by the Fermi-Dirac probability of finding an electron with the energy $\mathbf{E}$ and by integration over the whole set of electron states in the metal:

$$\frac{k_{\mu\nu}}{k_{\infty,\mu\nu}} = \frac{\int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{\left(\lambda + (\mathbf{E} - \mathbf{E}_F) + (\mathbf{E}_{1/2} - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right)^2}{4\lambda RT}\right] \exp\left(\frac{-\alpha_{\mu\nu}\Delta\mathbf{E}}{RT}\right)}{1 + \exp(\zeta)} d\zeta}{\lim(\mathbf{E}_F - \mathbf{E} \gg \lambda) \int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{\left(\lambda + (\mathbf{E} - \mathbf{E}_F) + (\mathbf{E}_{1/2} - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right)^2}{4\lambda RT}\right]}{1 + \exp(\zeta)} d\zeta}$$

where $k_{\infty,\mu\nu}$ is the maximal rate constant, ρ is the density of states corresponding to the energy $\mathbf{E}$ and $\mathbf{E}_F$ is the Fermi level energy. Assuming that $\chi_{\mu\nu}$ and the density of state are independent of the energy of the electronic states, and introducing:

$$\zeta = -\frac{\mathbf{E} - \mathbf{E}_F}{RT}$$

$$\frac{k_{\mu\nu}}{k_{\infty,\mu\nu}} = \frac{\int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{RT}{4\lambda} \left[\frac{1}{RT} \left(\lambda + (\mathbf{E}_{1/2} - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right) - \zeta\right]^2\right] \exp\left(\frac{-\alpha_{\mu\nu}(\mathbf{E}_F - \mathbf{E}_{1/2})}{RT}\right)}{1 + \exp(\zeta)} d\zeta}{\lim(\mathbf{E}_F - \mathbf{E} \gg \lambda) \int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{RT}{4\lambda} \left[\frac{1}{RT} \left(\lambda + (\mathbf{E}_F - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right) - \zeta\right]^2\right]}{1 + \exp(\zeta)} d\zeta}$$

With an appropriate change of integration variable, it can be shown that:

$$\lim(\mathbf{E}_F - \mathbf{E} \gg \lambda) \int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{RT}{4\lambda} \left[\frac{1}{RT} \left(\lambda + (\mathbf{E}_F - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right) - \zeta\right]^2\right]}{1 + \exp(\zeta)} d\zeta = \sqrt{\frac{4\pi\lambda}{RT}}$$

and thus

$$\frac{k_{\mu\nu}}{k_{\infty,\mu\nu}} = \sqrt{\frac{RT}{4\pi\lambda}} \int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{RT}{4\lambda} \left[\frac{1}{RT} \left(\lambda + (\mathbf{E}_{1/2} - \mathbf{E}_{00}^0) + w_{P,\nu} - w_{R,\mu}\right) - \zeta\right]^2\right] \exp\left(\frac{-\alpha_{\mu\nu}(\mathbf{E}_F - \mathbf{E}_{1/2})}{RT}\right)}{1 + \exp(\zeta)} d\zeta$$

with

$$k_{\infty,\mu\nu} = Z_{el} \chi_{\mu\nu} \exp\left[-\frac{w_{R,\mu}}{RT}\right] \exp\left(\frac{-(2\mu+1)\Delta ZPE}{RT}\right) = Z_{\mu\nu} \exp\left[-\frac{w_{R,\mu}}{RT}\right] \exp\left(\frac{-(2\mu+1)\Delta ZPE}{RT}\right)$$

Then,

$$k_{\mu\nu} = \left\{ Z_{el} \chi_{\mu\nu} \sqrt{\frac{RT}{4\pi\lambda}} \int_{-\infty}^{+\infty} \frac{\exp\left[-\frac{RT}{4\lambda} \left[\frac{\lambda + (\mathbf{E}_{1/2} - \mathbf{E}_{00}^0 + w_{P,\nu} - w_{R,\mu})}{RT} - \zeta\right]^2\right]}{1 + \exp(\zeta)} d\zeta \right\} \exp\left(\frac{-\alpha_{\mu\nu}\Delta\mathbf{E}}{RT}\right) \exp\left(-\frac{w_{R,\mu}}{RT}\right) \exp\left(\frac{-(2\mu+1)\Delta ZPE}{RT}\right)$$

Taking into account that $\mathbf{E}_F = -FE$, $\mathbf{E}_{1/2} = -FE_{1/2}$ and $\mathbf{E}_{00}^0 = -FE^0$,

$$k_{\mu\nu} = \left\{ Z_{el} \chi_{\mu\nu} \sqrt{\frac{RT}{4\pi\lambda}} \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda - F(E_{1/2} - E^0) + w_{P,\mu} - w_{R,\nu}}{RT} - \zeta \right]^2 \right]}{1 + \exp(\zeta)} d\zeta \right\} \exp \left[\frac{\alpha_{\mu\nu} F \Delta E}{RT} \right] \exp \left(-\frac{w_{R,\mu}}{RT} \right) \exp \left(\frac{-(2\mu+1)\Delta ZPE}{RT} \right)$$

This relation can be written:

$$k_{\mu\nu}(E) = Z_{el} \chi_{\mu\nu} \sqrt{\frac{RT}{4\pi\lambda}} I_{\mu\nu}(E_{1/2}) \exp \left(-\frac{w_{R,\mu}}{RT} \right) \exp \left(\frac{-(\mu+1)\Delta ZPE}{RT} \right) \exp \left[\frac{\alpha_{\mu\nu} F (E - E_{1/2})}{RT} \right]$$

with

$$I_{\mu\nu}(E_{1/2}) = \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda - F(E_{1/2} - E^0) + w_{P,\nu} - w_{R,\mu}}{RT} - \zeta \right]^2 \right]}{1 + \exp(\zeta)} d\zeta$$

Note that if $E_{1/2} \approx E^0$,

$$k_{\mu\nu}(E^0) = Z_{el} \chi_{\mu\nu} \sqrt{\frac{RT}{4\pi\lambda}} I_{\mu\nu}(E^0) \exp \left(-\frac{w_{R,\mu}}{RT} \right) \exp \left(\frac{-(2\mu+1)\Delta ZPE}{RT} \right) = k_{\mu\nu}^{S,ap}$$

with

$$I_{\mu\nu}(E^0) = \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda + w_{P,\nu} - w_{R,\mu}}{RT} - \zeta \right]^2 \right]}{1 + \exp(\zeta)} d\zeta$$

$$\begin{aligned} I_{\mu\nu}(E^0) &= \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\left(\frac{\lambda}{RT} - \zeta \right) + \frac{w_{P,\nu} - w_{R,\mu}}{RT} \right]^2 \right]}{1 + \exp(\zeta)} d\zeta = \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda}{RT} - \zeta \right]^2 \left[1 + \frac{w_{P,\nu} - w_{R,\mu}}{\left(\frac{\lambda}{RT} - \zeta \right) RT} \right]^2 \right]}{1 + \exp(\zeta)} d\zeta \\ &\approx \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda}{RT} - \zeta \right]^2 \left[1 + 2 \frac{w_{P,\nu} - w_{R,\mu}}{\left(\frac{\lambda}{RT} - \zeta \right) RT} \right] \right]}{1 + \exp(\zeta)} d\zeta \\ &\approx \exp \left[-\alpha \frac{(w_{P,\nu} - w_{R,\mu})}{RT} \right] \int_{-\infty}^{+\infty} \frac{\exp \left[-\frac{RT}{4\lambda} \left[\frac{\lambda}{RT} - \zeta \right]^2 \right]}{1 + \exp(\zeta)} d\zeta \end{aligned}$$

$$\text{if } \lambda > 10RT \quad I_{\mu\nu}(E^0) \approx \pi \exp \left(-\frac{\lambda}{4RT} \right) \exp \left[-\alpha \frac{(w_{P,\nu} - w_{R,\mu})}{RT} \right]$$

Thus,

$$k(E) = \frac{1}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_R}{RT}\right)} \sum_{\mu} \sum_{\nu} k_{\mu\nu}$$

$$= \left\{ Z_{el} \sqrt{\frac{RT}{4\pi\lambda}} \pi \exp\left(-\frac{\lambda}{4RT}\right) \frac{1}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_R}{RT}\right)} \sum_{\mu} \sum_{\nu} \chi_{\mu\nu} \exp\left[-\alpha \frac{(w_{P,\nu} - w_{R,\mu})}{RT}\right] \exp\left(-\frac{w_{R,\mu}}{RT}\right) \exp\left(-\frac{(2\mu+1)\Delta ZPE}{RT}\right) \right\} \exp\left[\frac{\alpha_{\mu\nu} F(E - E^0)}{RT}\right]$$

If $\alpha_{\mu\nu} \approx \alpha$ then

$$k(E) = \left\{ Z_{el} \sqrt{\frac{RT}{4\pi\lambda}} \pi \exp\left(-\frac{\lambda}{4RT}\right) \exp\left(-\frac{\Delta ZPE}{RT}\right) \frac{\sum_{\mu} \sum_{\nu} \chi_{\mu\nu} \exp\left[-\alpha \frac{(w_{P,\nu} - w_{R,\mu})}{RT}\right] \exp\left(-\frac{w_{R,\mu}}{RT}\right) \exp\left(-\frac{2\mu\Delta ZPE}{RT}\right)}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_R}{RT}\right)} \right\} \exp\left[\frac{\alpha F(E - E^0)}{RT}\right]$$

we find a typical Volmer expression for the rate constant and the relationship between $k^{S,ap}$ and Z :

$$k^{S,ap} \approx Z_{el} \sqrt{\frac{RT}{4\pi\lambda}} \pi \exp\left(-\frac{\lambda}{4RT}\right) \exp\left(-\frac{\Delta ZPE}{RT}\right) \frac{\sum_{\mu} \sum_{\nu} \chi_{\mu\nu} \exp\left[-\alpha \frac{(w_{P,\nu} - w_{R,\mu})}{RT}\right] \exp\left(-\frac{w_{R,\mu}}{RT}\right) \exp\left(-\frac{2\mu\Delta ZPE}{RT}\right)}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_R}{RT}\right)}$$

with

$$w_{R,\mu} = w_{R,0} + \mu \hbar \omega_R = z_R F \phi_S + \mu \hbar \omega_R$$

$$w_{P,\nu} = w_{P,0} + \nu \hbar \omega_P = (z_R + 1) F \phi_S + \nu \hbar \omega_P$$

ϕ_S is the double layer potential

If we take $\hbar \omega_R = \hbar \omega_P = \hbar \omega_0$

$$k^{S,ap} \approx Z_{el} \sqrt{\frac{RT}{4\pi\lambda}} \pi \exp\left(-\frac{\lambda + 4(\alpha + z_R) F \phi_S + 4\Delta ZPE}{4RT}\right) \left[\frac{\sum_{\mu} \sum_{\nu} \chi_{\mu\nu} \exp\left[-\alpha \frac{(\nu - \mu) \hbar \omega_0}{RT}\right] \exp\left(-\frac{\mu \hbar \omega_0}{RT}\right) \exp\left(-\frac{2\mu\Delta ZPE}{RT}\right)}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_0}{RT}\right)} \right]$$

Finally,

$$k^{S,ap} \approx Z_{el} \chi^{ap} \sqrt{\frac{RT}{4\pi\lambda}} \pi \exp\left(-\frac{\lambda + 4(\alpha + z_R) F \phi_S + 4\Delta ZPE}{4RT}\right)$$

with

$$\chi^{ap} \approx \left[\frac{\sum_{\mu} \sum_{\nu} \chi_{\mu\nu} \exp\left[-\alpha \frac{(\nu - \mu) \hbar \omega_0}{RT}\right] \exp\left(-\frac{\mu \hbar \omega_0}{RT}\right) \exp\left(-\frac{2\mu\Delta ZPE}{RT}\right)}{\sum_{\mu} \exp\left(-\frac{\mu \hbar \omega_0}{RT}\right)} \right]$$

Note that χ^{ap} may be greater than 1.

If only vibrational ground states are considered, then $\chi^{ap} \approx \chi_{00}$.

4. Isosceles triangular proton potential model

Fig. 3S. Triangular approximation of the proton potential profile.

Expression of the proton potential:

For $d_{OH}^0 \leq q \leq q^{\ddagger}$: $V = A(q - d_{OH}^0)$, for $q^{\ddagger} \leq q \leq Q - d_{NH}^0$: $V = -A(q - Q + d_{NH}^0)$

d_{OH}^0 and d_{NH}^0 are the proton equilibrium distances in the reactant and product respectively; Q is defined as the sum of O-H and N-H distances.

$$q^{\ddagger} = \frac{Q - d_{NH}^0 + d_{OH}^0}{2}$$

Assuming that the slope of proton potential is such as the linear proton potential crosses harmonic potential at an energy value equal to half of the proton activation barrier (figure 3S):

$$\frac{\Delta V^{\ddagger}}{2} = A(q' - d_{OH}^0) = \frac{f_0^{\ddagger}}{2}(q' - d_{OH}^0)^2$$

Thus, the slope of proton potential is:

$$A = \frac{f_0^{\ddagger}}{2}(q' - d_{OH}^0) = \frac{f_0^{\ddagger}}{2}\left(\frac{q^{\ddagger} - d_{OH}^0}{2}\right) = \frac{f_0^{\ddagger}}{8}\left(\frac{Q - d_{NH}^0 - d_{OH}^0}{4}\right)$$

where $f_0^{\ddagger} = 4\pi^2\nu_0^{\ddagger 2} m_p$ is the force constant of the proton vibration and the proton barrier height:

$$\Delta V^{\ddagger} = A(q^{\ddagger} - d_{OH}^0) = \frac{f_0^{\ddagger}}{4}\left(\frac{Q - d_{NH}^0 - d_{OH}^0}{2}\right)^2$$

Coupling constant:

$$C(Q) = h\nu_0^{\ddagger} \exp\left[-\frac{2\pi}{h} \int_{q_i}^{q_f} \sqrt{2m_p \left(V(q, Q) - \frac{h\nu_0^{\ddagger}}{2}\right)} dq\right]$$

m_p : proton mass, q_i and q_f : classical turning points in each well at fixed Q

Turning points:

$$A(q_i - d_{OH}^0) = \frac{h\nu_0^{\ddagger}}{2} \text{ and } A(Q - q_f - d_{NH}^0) = \frac{h\nu_0^{\ddagger}}{2}$$

thus:

$$q_i = d_{OH}^0 + \frac{h\nu_0^{\ddagger}}{2A} \text{ and } q_f = Q - d_{NH}^0 - \frac{h\nu_0^{\ddagger}}{2A}$$

It follows that:

$$\begin{aligned}
\frac{2\pi}{h} \int_{q_i}^{q_f} \sqrt{2m_p \left(V(q, Q) - \frac{hv_0^\#}{2} \right)} dq &= \frac{2\pi\sqrt{2m_p}A}{h} \left(\int_{q_i}^{q^\#} \sqrt{V(q, Q) - \frac{hv_0^\#}{2}} dq + \int_{q^\#}^{q_f} \sqrt{V(q, Q) - \frac{hv_0^\#}{2}} dq \right) \\
&= \frac{2\pi\sqrt{2m_p}A}{h} \left(\int_{q_i}^{q^\#} \sqrt{\left(q - d_{OH}^0 \right) - \frac{hv_0^\#}{2A}} dq + \int_{q^\#}^{q_f} \sqrt{\left(q - Q + d_{NH}^0 \right) - \frac{hv_0^\#}{2A}} dq \right) \\
&= \frac{2\pi\sqrt{2m_p}A}{h} \left(\int_{q_i}^{q^\#} \sqrt{q - d_{OH}^0 - \frac{hv_0^\#}{2A}} dq + \int_{q^\#}^{q_f} \sqrt{Q - q - d_{NH}^0 - \frac{hv_0^\#}{2A}} dq \right)
\end{aligned}$$

Introducing :

$$u = q - d_{OH}^0 - \frac{hv_0^\#}{2A} \quad \text{and} \quad v = Q - q - d_{NH}^0 - \frac{hv_0^\#}{2A}$$

$$\begin{aligned}
\frac{2\pi}{h} \int_{q_i}^{q_f} \sqrt{2m_p \left(V(q, Q) - \frac{hv_0^\#}{2} \right)} dq &= \frac{\sqrt{2m_p}A}{h} \left(\int_{q_i - d_{OH}^0 - \frac{hv_0^\#}{2A}}^{q^\# - d_{OH}^0 - \frac{hv_0^\#}{2A}} \sqrt{u} du - \int_{Q - q^\# - d_{NH}^0 - \frac{hv_0^\#}{2A}}^{Q - q_f - d_{NH}^0 - \frac{hv_0^\#}{2A}} \sqrt{v} dv \right) \\
&= \frac{\sqrt{2m_p}A}{h} \left(\int_0^{q^\# - d_{OH}^0 - \frac{hv_0^\#}{2A}} \sqrt{u} du + \int_0^{Q - q^\# - d_{NH}^0 - \frac{hv_0^\#}{2A}} \sqrt{v} dv \right) = \frac{\sqrt{2m_p}A}{h} \left(\int_0^{\frac{Q - d_{NH}^0 - d_{OH}^0}{2} - \frac{hv_0^\#}{2A}} \sqrt{u} du + \int_0^{\frac{Q - d_{NH}^0 - d_{OH}^0}{2} - \frac{hv_0^\#}{2A}} \sqrt{v} dv \right) \\
&= 2 \frac{\sqrt{2m_p}A}{h} \int_0^{\frac{Q - d_{NH}^0 - d_{OH}^0}{2} - \frac{hv_0^\#}{2A}} \sqrt{u} du = \frac{4\sqrt{2m_p}A}{3h} \left(\frac{Q - d_{NH}^0 - d_{OH}^0}{2} - \frac{hv_0^\#}{2A} \right)^{3/2} = \frac{8\sqrt{2}}{3} \sqrt{\frac{hv_0^\#}{\Delta V^\#}} \left(\frac{\Delta V^\#}{hv_0^\#} - \frac{1}{2} \right)^{3/2}
\end{aligned}$$

It follows that:

$$C(Q) = hv_0^\# \exp \left[-\frac{8\sqrt{2}}{3} \sqrt{\frac{hv_0^\#}{\Delta V^\#}} \left(\frac{\Delta V^\#}{hv_0^\#} - \frac{1}{2} \right)^{3/2} \right] \quad (\text{equation 15}).$$

5. Triangular proton potential model in presence of an electric field

Fig. 4S. Triangular approximation of the proton potential profile.

5.1. Expression of the proton potential

For $d_{OH}^0 \leq q \leq q^\#$: $V = V_R = B(q - d_{OH}^0)$, for $q^\# \leq q \leq Q - d_{NH}^0$: $V = V_P = -A(q - Q + d_{NH}^0)$

$$\text{Thus: } q^\# = \frac{A(Q - d_{NH}^0) + Bd_{OH}^0}{A + B}$$

Slope ratio:

$$\frac{B}{A} = \frac{\Delta V^\# - \Delta E}{\Delta V^\# + \Delta E}$$

Classical turning points in each well at fixed Q , q_i' and q_f :

$$B(q_i' - d_{\text{OH}}^0) = \frac{h\nu_0^\ddagger}{2} \text{ and } A(Q - q_f - d_{\text{NH}}^0) = \frac{h\nu_0^\ddagger}{2}$$

5.2. Coupling constant

$$C(Q) = h\nu_0^\ddagger \exp \left[-\frac{1}{\hbar} \int_{q_i'}^{q_f} \sqrt{2m_p \left(V(q, Q) - \frac{h\nu_0^\ddagger}{2} \right)} dq \right]$$

$$\frac{2\pi}{\hbar} \int_{q_i'}^{q_f} \sqrt{2m_p \left(V(q, Q) - \frac{h\nu_0^\ddagger}{2} \right)} dq = \frac{2\pi\sqrt{2m_p B}}{\hbar} \left[\int_{q_i'}^{q^{\ddagger}} \sqrt{q - d_{\text{OH}}^0 - \frac{h\nu_0^\ddagger}{2B}} dq \right] + \frac{\sqrt{2m_p A}}{\hbar} \left[\int_{q^{\ddagger}}^{q_f} \sqrt{Q - q - d_{\text{NH}}^0 - \frac{h\nu_0^\ddagger}{2A}} dq \right]$$

Following the same calculation as in the previous section, we found:

$$C_{\text{ef}}(Q) = h\nu_0^\ddagger \exp \left\{ -\frac{2\sqrt{2}}{3} \frac{f_0^\ddagger}{h\nu_0^\ddagger} \left[\sqrt{B} \left(q^{\ddagger} - d_{\text{OH}}^0 - \frac{h\nu_0^\ddagger}{2B} \right)^{3/2} + \sqrt{A} \left(Q - q^{\ddagger} - d_{\text{NH}}^0 - \frac{h\nu_0^\ddagger}{2A} \right)^{3/2} \right] \right\} \quad (\text{equation 17})$$

6. Calculation of $\hbar\omega_Q$

The potential energy profile of the reactant is calculated as a function of a distance Q (figure 5S). This distance Q is defined as the sum of O-H and N-H distances and is referred as the “proton donor-acceptor distance”. Fitting this profile with a quadratic function around the energy minimum allows determination of $h\nu_Q = 0.0817$ eV ($m_Q = 7.5$ amu).

Figure 5S. Reactant energy profile as a function of the proton donor-acceptor distance Q .

References and Notes

- 1S. Soudackov, A.; Hatcher, E.; Hammes-Schiffer, S. *J. Chem. Phys.* **2005**, *122*, 014505.
- 2S. Borgis, D.; Hynes J. T. *Chem. Phys.* **1993**, *170*, 315.
- 3S. Hatcher, E.; Soudackov, A.; Hammes-Schiffer, S. *J. Phys. Chem. B* **2005**, *109*, 18565.
- 4S. (a) Hatcher, E.; Soudackov, A.; Hammes-Schiffer, S. *Chem. Phys.* **2005**, *319*, 93. (b) Hatcher, E.; Soudackov, A.; Hammes-Schiffer, S. *J. Am. Chem. Soc.* **2007**, *129*, 187.
- 5S. Borgis, D.; Hynes J. T. *Chem. Phys. Lett.* **1989**, *162*, 19.

Complete ref 36:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, M. A.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, G.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, A. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*, Revision A.1; Gaussian, Inc. : Pittsburgh, PA, 1998.