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Concerted Proton−Electron Transfer Reactions in Water. Are the Driving Force and Rate Constant Depending on pH When Water Acts as Proton Donor or Acceptor?

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Abstract: The competition between stepwise and concerted (CPET) pathways in proton-coupled electron-transfer reactions in water is discussed on thermodynamic and kinetic bases. In the case where water is the proton acceptor, the CPET pathway may compete favorably with the stepwise pathway. The main parameter of the competition is pK of the oxidized form of the substrate being smaller or larger than 0. The driving force of the forward reaction is however independent of pH, despite the equilibrium redox potential of the proton−electron system being a function of pH. At high pH values, CPET reactions involving OH^- as proton acceptor may likewise compete favorably with stepwise pathways. The overall reaction rate constant is an increasing function of pH, not because the driving force depends on pH but because OH^- is a reactant. In buffered media, association of the substrate with the basic components of the buffer offers an alternative CPET route; the driving force comes closer to that offered by the pH-dependent equilibrium redox potential.

Introduction

Proton-coupled electron transfers (PCET) where proton and electron transfer involves different molecular centers is a central problem of chemical reactivity, which attracts additional active attention in view of the involvement of these processes in many natural processes.[1] Particular emphasis has been laid on the possibility that the two steps be concerted giving rise to a CPET (for concerted proton−electron transfer) reaction. Several homogeneous or electrochemical systems have been investigated in view of illustrating the occurrence of CPET pathways, rather than the competing stepwise pathways (Scheme 1), which involve the transfer of an electron followed by the transfer of a proton (ETPT) and/or the reversed sequence (PTET). One category concerns intramolecular PCET reactions, typically involving an amine or a carboxylate as proton accepting center.[2] Another group consists of intermolecular reactions involving the prior formation of a H-bonded complex.[3] A third type of particularly interesting PCET reactions, carried out in water, comprises those in which water may act as the proton acceptor. This role may also be played by OH^- and by the basic components of buffers in which the experiments are often carried out. In this connection, the oxidation of the phenol group of tyrosine has attracted particular attention[4−6] in view of its role in the reactions taking place in photosystem II[1f−g] and in other biosystems such as ribonucleotide reductases.[1b,c,7] While in both cases the contribution of the CPET pathway is deemed important, conflicting evidence has been reported concerning the respective role of water[5] and of the basic component of the buffer[6] as proton acceptors. The key observation of an alleged lack of dependence of the rate constant on the buffer concentra-

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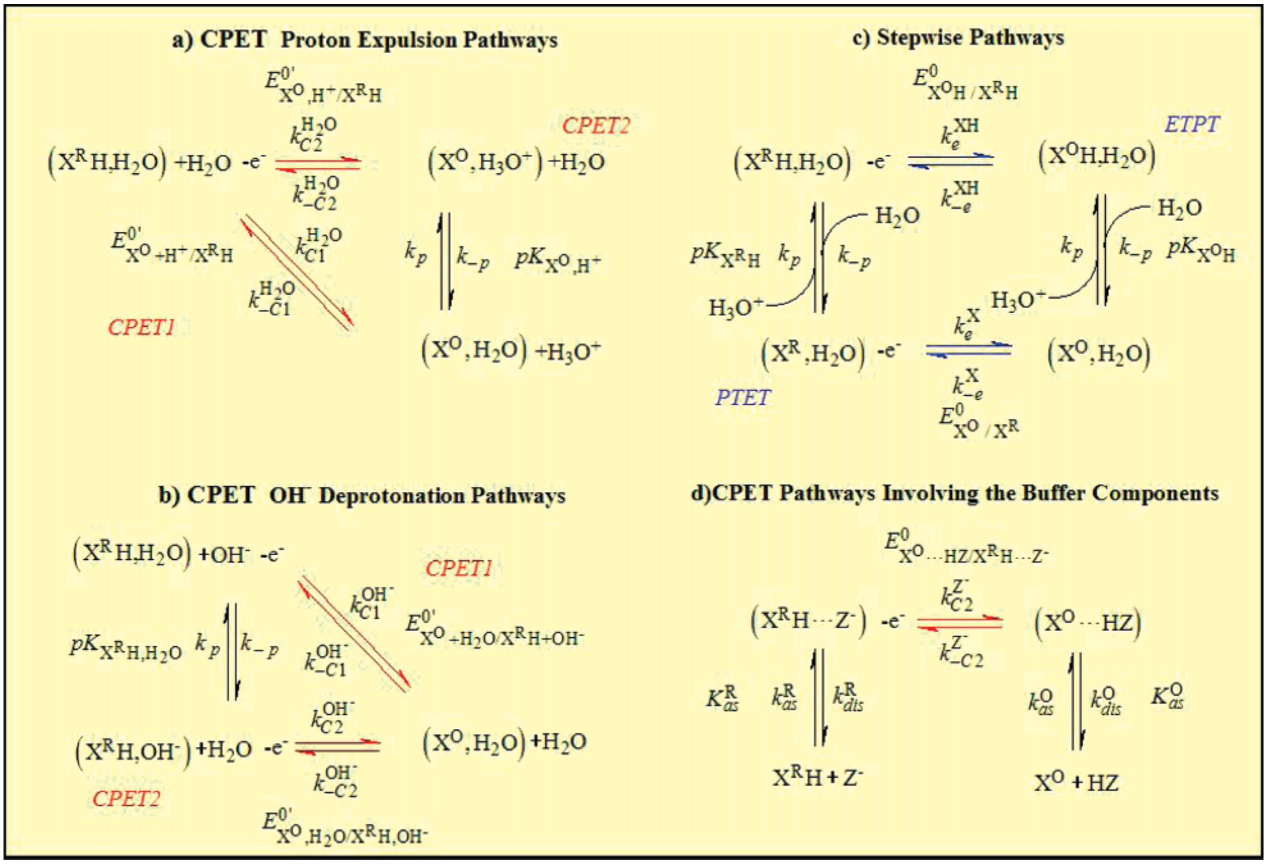
Scheme 1



tion or even of its presence reported in reference 5 is indeed challenged by the results in reference 6 which describe an exactly opposite behavior. In the first case, the results, in particular the variation of the observed rate constant with pH, in the absence of buffer, have been rationalized by considering that the driving force of the CPET reaction is an increasing function of pH.[5,8] Introduction of this pH-dependent driving force into the Marcus activation-driving force relationship, assumed to be applicable to CPET reactions, would then account for the increase of the rate constant with pH.

Assessing the role of water in CPET reactions is important from a fundamental point of view and also for gaining further insights into their mechanisms in biological processes. The various expected stepwise and CPET reaction pathways are summarized in Scheme 1 (simple outersphere electron transfers in blue, concerted proton−electron transfer in red). We will start the discussion with the case where water is the proton acceptor in the CPET reaction and show that the rate constant of such water-assisted reactions is not a function of pH. The conditions under which such CPET pathways may surpass a stepwise pathway in which the electron is transferred first, followed by the transfer of a proton, (ETPT) will be established. We will then discuss the occurrence of CPET reactions in which OH^- is the proton acceptor and show that the rate constant is independent of pH too. The conditions under which these CPET pathways may surpass a stepwise pathway in which the proton is transferred first, followed by the transfer of one electron (PTET) will then be established. Finally, CPET reactions involving buffer components will be discussed. Although the driving force and the rate constant, for each buffer component, still do not vary with pH, the observed overall rate constant may well vary with pH upon changing the buffer composition.

Results and Discussion

The species involved (Scheme 1), at the reduced (X^RH, X^R) and oxidized (X^OH, X^O) states, are considered as being clustered with water molecules, one of which may serve as proton donor or acceptor. This is the water molecule shown in the schemes. The various thermodynamic constants, standard (or formal) potentials, pK values and association constants are defined together with the schemes representing the reaction pathways. The notations involve as lower index a simplified designation of the reaction under consideration. We focus on reactions where the substrate is oxidized by means of an appropriate outersphere electron acceptor. Extension to the opposite case of a substrate reduction involving an outersphere electron donor is straightforward.

1. Two-Step and One-Step CPET-H_2O Pathways. We consider the following scenarios. In the two-step CPET2 scenario, the first step is a concerted proton−electron transfer, leading to proton formation, which takes place inside the water cluster. The proton thus formed is transferred into the bulk of the solution in a second step. Two cases are then distinguished according to whether the second step is so fast as to remain unconditionally at equilibrium or is governed by proton diffusion. The two reactions are concerted in the one-step CPET1 scenario. The CPET reaction then includes the proton diffusion process so as to deliver the proton directly in the bulk.

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1.1. Do Driving Forces and Rate Constants Depend on pH? The rate equations corresponding to the two-step reaction (CPET2 pathway in Scheme 1a) write

$$\frac{d[X^RH,H_2O]}{dt} = -k_{C2}^{H_2O}[X^RH,H_2O] + k_{-C2}^{H_2O}[X^O,H_3O^+]$$

$$\frac{d[X^O,H_3O^+]}{dt} = k_{C2}^{H_2O}[X^RH,H_2O] - k_{-C2}^{H_2O}[X^O,H_3O^+] - k_{-p}[H_2O][X^O,H_3O^+] + k_p[H_3O^+][X^O,H_2O]$$

$$\frac{d[X^O,H_2O]}{dt} = k_{-p}[H_2O][X^O,H_3O^+] - k_p[H_3O^+][X^O,H_2O]$$

where each [ ] represents the concentration of the bracketed species, and the rate constants are as marked in Scheme 1a.

The rate constant of the first step, $k_{C2}^{H_2O}$ may be expressed as a combination of the activation free energy, $\Delta G_{C2}^{H_2O\neq}$ and of the pre-exponential factor, $Z_{\text{mono or bi}}\ \chi_{C2}^{H_2O}$:

$$k_{C2}^{H_2O} = Z_{\text{mono or bi}}\ \chi_{C2}^{H_2O} \exp\left(-\frac{\Delta G_{C2}^{H_2O\neq}}{RT}\right)$$

$k_{C2}^{H_2O}$ and the collision factor $Z_{\text{mono or bi}}$ are monomolecular or bimolecular constants according to the electron acceptor being attached to the electron donor or freely diffusing in the solution. The transmission coefficient, $\chi_{C2}^{H_2O}$, is a measure of proton tunneling in the CPET2 reaction.

The Marcus quadratic equation[9] has often been used to relate activation and driving force in CPET reactions.[2a,b,5] More sophisticated and more exact treatments of the kinetics of CPET reactions are available,[10] which also relate activation to driving force. This is obtained from the formal potentials of the electron acceptor, $E_A^{0'}$ and of the first step, $E^{0'}_{X^O,H^+/X^RH}$:

$$\Delta G_{C2}^{H_2O0'} = F(E^{0'}_{X^O,H^+/X^RH} - E^{0'}_A)$$

where:

$$FE^{0'}_{X^O,H^+/X^RH} = \mu^{0'}_{X^O,H^+} - \mu^{0'}_{X^RH}$$

The symbols $\mu^{0'}$ represent, here and throughout the paper, the formal chemical potentials. They are related to the chemical potential by

$$\mu = \mu^{0'} + RT\ln[\ ] = \mu^0 + RT\ln(\gamma[\ ])$$

where μ^0 is the standard chemical potential and γ is the activity coefficient. With the exception of water, all standard states are defined by extrapolation of the ideal conditions at 1 M. For water, the standard state is the pure liquid. The $\mu^{0'}$ and the μ^0 values do not include a contribution from entropy of mixing of the reactants,[11] and therefore do not contain reactant concentration terms.

The pH does not interfere in the kinetics of the first step but may influence the kinetics of the overall two-step reaction. In this respect, a first interesting limiting situation is when the adduct formation and dissociation reactions are fast enough for the reaction to remain unconditionally at equilibrium. The kinetics then involves overall forward and backward rate constants, $k_{f,C2}^{H_2O}$ and $k_{b,C2}^{H_2O}$, defined by

$$\frac{d[X^RH,H_2O]}{dt} = -\frac{d([X^O,H_3O^+] + [X^O,H_2O])}{dt} = -k_{f,C2}^{H_2O}[X^RH,H_2O] + k_{b,C2}^{H_2O}([X^O,H_3O^+] + [X^O,H_2O])$$

where

$$k_{f,C2}^{H_2O} = k_{C2}^{H_2O}$$

$$k_{b,C2}^{H_2O} = k_{-C2}^{H_2O}\frac{10^{-pH}}{\dfrac{\gamma_{X^O,H_3O^+}}{\gamma_{X^O,H_2O}}10^{-pK_{X^O,H^+}} + 10^{-pH}}$$

where γ is the activity coefficient of the subscript species (taking for the activity of water, $\gamma_{H_2O}[H_2O] = 1$).

It follows that the observed forward rate constant is predicted to be independent of pH. The overall backward rate constant does depend on pH, according to the above equation, not because the second-order rate constant depends on pH but because the proton is a reactant in the backward process, namely in the formation of the proton adduct. This is in fact the way in which the proton mixing entropy, invoked in recent analyses of the problem to justify the notion of a pH-depending driving force,[5] interferes in the kinetics of the reaction.

In summary, the pseudo-first-order backward rate constant depends on pH as a reflection of the proton mixing entropy but the forward reaction rate constant does not.

We now lift the assumption that formation and decomposition of the H_3O^+ cluster are in unconditional equilibrium. To emphasize the mixing entropy aspect of the problem alluded to in reference 5, we assume that the interaction energy within the cluster is negligible so that the coming in and out of the proton can be viewed as a diffusion process, possibly involving an oxygen site-to oxygen site proton hopping according to a Grotthuss-type mechanism.[12] In the approximate spherical symmetry framework sketched in Figure 1, at steady state,

$$[H^+]_r = \frac{([H^+]_{r=R} - [H^+]_{r\to\infty})R}{r} + [H^+]_{r\to\infty}$$

$[H^+]_{r\to\infty}$ is the bulk concentration of proton. It is regarded as constant, even in unbuffered medium if the overall production of protons is small as compared to the amount of protons already present in the bulk even at high pH values. If this is not the case, we assume that proton concentration is maintained constant by the presence of a buffer which components do not participate to the CPET reaction as hypothesized in reference 5. The thickness of the diffusion layer is of the order of R, meaning that the bulk concentration is reached at small distances from the reaction center, thus involving a small number of water molecules. The proton flux at the surface of the sphere is expressed as

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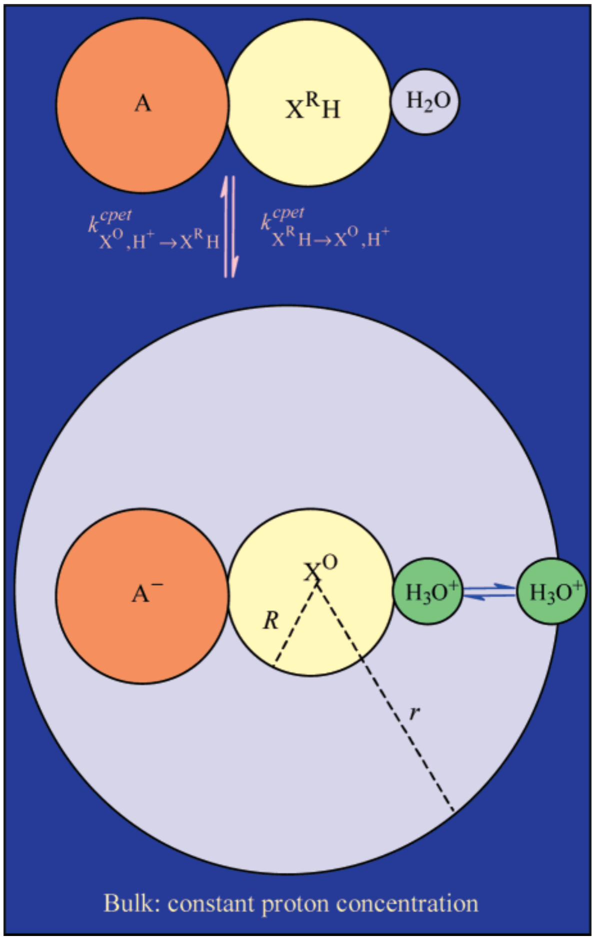

Figure 1. Two-step CPET proton expulsion reactions; follow-up proton diffusion.

$$-4\pi D_{H^+}\left(r^2\frac{d[H^+]}{dr}\right)_{r=R} = 4\pi D_{H^+} R([H^+]_{r=R} - [H^+]_{r\rightarrow\infty})$$

Thus, at the molar scale,

$$-\frac{d[X^RH,H_2O]}{dt} = \frac{d[X^O,H_3O^+]}{dt}$$

$$= k^{H_2O}_{C2}[X^RH,H_2O] - k^{H_2O}_{-C2}[H^+]_{r=R}[X^O]$$

$$= k_{dif,H^+}([H^+]_{r=R} - [H^+]_{r\rightarrow\infty})[X^O]$$

D_{H^+} is the proton diffusion coefficient, and $k_{dif,H^+} = 4\pi D_{H^+} RN_A$ (N_A = Avogadro number) is the proton diffusion limit.

It follows that

$$[H^+]_{r=R} = \frac{k_{dif,H^+}[H^+]_{r\rightarrow\infty}[X^O] + k^{H_2O}_{C2}[X^RH,H_2O]}{k_{dif,H^+}[X^O] + k^{H_2O}_{-C2}[X^O]}$$

In total, the governing rate equations become ($[H^+]_{r\rightarrow\infty}$ is equal to the value of $[H_3O^+]$ in the bulk)

$$-\frac{d[X^RH,H_2O]}{dt} = \frac{d[X^O,H_3O^+]}{dt} = k^{H_2O}_{f,C2}[X^RH,H_2O] - k^{H_2O}_{b,C2} \times 10^{-pH}[X^O]$$

where the overall rate constants are now defined by

$$\frac{1}{k^{H_2O}_{f,C2}} = \frac{1}{k^{H_2O}_{C2}} + \frac{1}{\exp\left[\frac{F}{RT}(E^{0'}_A - E^{0'}_{X^O,H^+/X^RH})\right]k_{dif,H^+}}$$

$$\frac{\gamma_{H_3O^+}}{k^{H_2O}_{b,C2}} = \frac{1}{k^{H_2O}_{-C2}} + \frac{1}{k_{dif,H^+}}$$

Proton diffusion does interfere in the second term of the expression of the forward rate constant but in a manner that is independent of pH. This second term vanishes when the electron acceptor is sufficiently strong an oxidant to make the reaction irreversible. As expected, pH interferes in the kinetics of the backward reaction inasmuch proton is a reactant of this reaction.

At this stage, we may conclude that, in all situations, the forward rate constant of CPET proton expulsion reactions is not expected to vary with pH, whereas the overall backward rate constant varies with pH because proton is a reactant in the backward process.

We may now go a step forward in terms of concertedness. In the above discussion, we have considered proton production and proton diffusion as two successive steps. We now regard these two steps as concerted: the CPET reaction now includes the proton diffusion process so as to produce directly bulk protons, even if there might be a price to pay for this in terms of reorganization energy and pre-exponential factor. If the oxygen site-to oxygen site proton hopping is concerted with electron transfer, we indeed expect an increase of the reorganization energy related to variations in the oxygen-to-oxygen distances and to the reorganization of water molecules not participating directly to the conducting chain.

The rate equation now writes

$$\frac{d[X^RH,H_2O]}{dt} = -k^{H_2O}_{C1}[H_2O][X^RH,H_2O] + k^{H_2O}_{-C1}[H_3O^+][X^O,H_2O]$$

The driving force, defined from

$$\Delta G^{H_2O^{0'}}_{C1} = F(E^{0'}_{X^O+H^+/X^RH} - E^{0'}_A)$$

is governed by the formal potential

$$FE^{0'}_{X^O+H^+/X^RH} = \mu^{O'}_{X^O} + \mu^{0'}_{H_3O^+} - \mu^{0'}_{X^RH} - \mu^{0'}_{H_2O}$$

which again does not depends on pH. Indeed, as in the preceding case of one reactant and one product, the $\mu^{0'}$ values do not include a contribution from the entropy of mixing of the reactants, and therefore do not contain reactant concentration terms. This conclusion has been previously reached for electron-transfer reactions involving more than one reactant and one product, in the case of dissociative electron transfers[13] and, more recently, in the case of proton coupled electron transfers.[14] As noted before, the validity of this conclusion does not require a quadratic activation−driving force relationship.

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The overall forward and backward rate constants, $k_{\mathrm{f,C1}}^{\mathrm{H_2O}}$ and $k_{\mathrm{b,C1}}^{\mathrm{H_2O}}$ are defined by

$$\frac{\mathrm{d}[\mathrm{X^RH,H_2O}]}{\mathrm{d}t} = -k_{\mathrm{f,C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}][\mathrm{X^RH,H_2O}] + k_{\mathrm{b,C1}}^{\mathrm{H_2O}} \times 10^{-\mathrm{pH}}[\mathrm{X^O,H_2O}]$$

with

$$k_{\mathrm{f,C1}}^{\mathrm{H_2O}} = k_{\mathrm{C1}}^{\mathrm{H_2O}}$$

$$k_{\mathrm{b,C1}}^{\mathrm{H_2O}} = \frac{k_{-\mathrm{C1}}^{\mathrm{H_2O}}}{\gamma_{\mathrm{H_3O^+}}} 10^{-\mathrm{pH}}$$

The forward rate constant may be expressed as

$$k_{\mathrm{f,C1}}^{\mathrm{H_2O}} = k_{\mathrm{C1}}^{\mathrm{H_2O}} = Z_{\text{bi or ter}}\, \chi_{\mathrm{C1}}^{\mathrm{H_2O}} \exp\left(-\frac{\Delta G_{\mathrm{C1}}^{\mathrm{H_2O}\neq}}{RT}\right)$$

where $\Delta G_{\mathrm{C1}}^{\mathrm{H_2O}\neq}$ is the activation free energy and $k_{\mathrm{C1}}^{\mathrm{H_2O}}$ and $Z_{\text{bi or ter}}$ are bimolecular or termolecular rate constants according to the electron acceptor being attached to the electron donor or freely diffusing in the solution. The transmission coefficient, $\chi_{\mathrm{C1}}^{\mathrm{H_2O}}$, is a measure of proton tunneling in the CPET reaction.

The kinetics of the forward reaction does not thus depend on pH, in line with the fact that the driving force does not depend on pH either, even though the entropy increase related to proton diffusion has duly been taken into account. The overall rate constant of backward reaction does depend on pH, not because the second-order rate constant depends on pH but simply because the proton is a reactant in the backward reaction.

We may thus conclude that whether the CPET proton expulsion reaction follows this concerted process or the two-step scenarios discussed earlier, the driving force is independent of pH and so is the forward rate constant.

An objection to this conclusion might be that the reactivity (and activity) of the water molecules involved in the CPET reaction could depend on the bulk concentration of protons. Such an effect, if any, would fit the framework of the third scenario we discussed above in which the proton is released to the bulk along short water chains concertedly with electron transfer. In an a fortiori approach, we may regard the last water molecule in the chain, say the fifth one, as being unable to accept a proton because it is already bonded to a proton, thus blocking the reaction. The influence of the proton on the reactivity is expected to vanish upon increasing its average distance to the reactant. It is reasonable to estimate that this influence has become totally negligible at a distance corresponding to ten water molecules. Among the ca. 50 mol of water molecules in a liter, the protonation of 5 mol of them would thus be required to start affecting the reaction rate. This effect is obviously negligible over the usual pH ranges where the experiments are carried out.

1.2. Competition between CPET Proton Expulsion and Stepwise ETPT Pathways. Insofar as the oxidation reactions are irreversible, as it is usually in experimental studies,[5,6] predicting the outcome of the competition between the title concerted and stepwise pathways amounts to a comparison of $k_{\mathrm{f,C1}}^{\mathrm{H_2O}} \times [\mathrm{H_2O}]$ or $k_{\mathrm{f,C2}}^{\mathrm{H_2O}}$ with $k_{\mathrm{e}}^{\mathrm{XH}}$.

As a gross approximation, the activation free energies may be related to the driving force by a linear relationship with a symmetry factor of 1/2. Then

$$\Delta G_{\mathrm{C1}}^{\mathrm{H_2O}\neq} \simeq \frac{\lambda_{\mathrm{C1}}^{\mathrm{H_2O}}}{4} + F\,\frac{E^{0'}_{\mathrm{X^O+H^+/X^RH}} - E^{0'}_{\mathrm{A}}}{2}$$

$$\Delta G_{\mathrm{C2}}^{\mathrm{H_2O}\neq} \simeq \frac{\lambda_{\mathrm{C2}}^{\mathrm{H_2O}}}{4} + F\,\frac{E^{0'}_{\mathrm{X^O,H^+/X^RH}} - E^{0'}_{\mathrm{A}}}{2}$$

and for the first step outersphere electron transfer in the ETPT pathway (where λ is are the corresponding reorganization energy)

$$\Delta G_{\mathrm{e}}^{\mathrm{XH}\neq} \simeq \frac{\lambda^{\mathrm{XH}}}{4} + F\,\frac{E^{0'}_{\mathrm{X^OH/X^RH}} \text{ - } E^{0'}_{\mathrm{A}}}{2}$$

Still concerning the ETPT first step,

$$k_{\mathrm{e}}^{\mathrm{XH}} = Z_{\text{mono or bi}}\kappa^{\mathrm{XH}} \exp\left(-\frac{\Delta G_{\mathrm{e}}^{\mathrm{XH}\neq}}{RT}\right)$$

where κ^{XH} is the transmission coefficient for this outersphere electron-transfer reaction.

The comparison between the two pathways may thus be formulated as

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{k_{\mathrm{e}}^{\mathrm{XH}}}\right) \simeq \log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{Z_{\text{mono or bi}}\kappa^{\mathrm{XH}}}\right) - \frac{\lambda_{\mathrm{C1}}^{\mathrm{H_2O}} - \lambda^{\mathrm{XH}}}{4RT\ln 10} + \frac{F}{RT\ln 10}\,\frac{E^{0'}_{\mathrm{X^OH/X^RH}} - E^{0'}_{\mathrm{X^O+H^+/X^RH}}}{2}$$

$$FE^{0'}_{\mathrm{X^O+H^+/X^RH}} = \mu^{0'}_{\mathrm{X^O}} + \mu^{0'}_{\mathrm{H_3O^+}} - \mu^{0'}_{\mathrm{X^RH}} - \mu^{0'}_{\mathrm{H_2O}}$$

and

$$FE^{0'}_{\mathrm{X^OH/X^RH}} = \mu^{0'}_{\mathrm{X^OH}} - \mu^{0'}_{\mathrm{X^RH}}$$

Thus,

$$E^{0'}_{\mathrm{X^OH/X^RH}} - E^{0'}_{\mathrm{X^O+H^+/X^RH}} = \frac{RT\ln 10}{F}\log\left(\frac{\gamma_{\mathrm{X^OH}}\gamma_{\mathrm{H_2O}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_3O^+}}}\right) - \frac{RT\ln 10}{F}\,\mathrm{p}K_{\mathrm{X^OH}}$$

and

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{k_{\mathrm{e}}^{\mathrm{XH}}}\right) \simeq \log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{Z_{\text{mono or bi}}\kappa^{\mathrm{XH}}}\right) + \frac{\lambda^{\mathrm{XH}} - \lambda_{\mathrm{C1}}^{\mathrm{H_2O}}}{4RT\ln 10} + \frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^OH}}\gamma_{\mathrm{H_2O}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_3O^+}}}\right) - \frac{1}{2}\,\mathrm{p}K_{\mathrm{X^OH}}$$

and therefore, taking into account that $\gamma_{\mathrm{H_2O}}[\mathrm{H_2O}] = 1$:

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{k_{\mathrm{e}}^{\mathrm{XH}}}\right) \simeq \log\left(\frac{\chi_{\mathrm{C1}}^{\mathrm{H_2O}}}{\kappa^{\mathrm{XH}}}\,\frac{Z_{\text{bi or ter}}[\mathrm{H_2O}]^{1/2}}{Z_{\text{mono or bi}}}\right) + \frac{\lambda^{\mathrm{XH}} - \lambda_{\mathrm{C1}}^{\mathrm{H_2O}}}{4RT\ln 10} + \frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^OH}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_3O^+}}}\right) - \frac{1}{2}\,\mathrm{p}K_{\mathrm{X^OH}}$$

The third term in the right-hand side is close to nil in the usual experimental pH ranges. The factor $Z_{\text{mono or bi}}/Z_{\text{bi or ter}} \simeq$

10−20[13b] is almost compensated by $[\mathrm{H_2O}]^{1/2} \simeq 7.5$. In addition, although not to a large extent, outersphere electron transfers are expected to be intrinsically more favorable than CPET reactions both in terms of reorganization ($\lambda_{\mathrm{C1}}^{\mathrm{H_2O}} < \lambda^{\mathrm{XH}}$) and transmission coefficient ($\chi_{\mathrm{C1}}^{\mathrm{H_2O}} < \kappa^{\mathrm{XH}}$) than CPET reactions (in the above equation the outersphere electron transfer is assumed to be adiabatic, i.e., its transmission coefficient is equal to 1). The main factor that governs the competition between the CPET1 and ETPT routes is thus the p*K* of $\mathrm{X^OH}$ being positive or negative.

Since

$$E^{0'}_{\mathrm{X^O,H^+/X^RH}} - E^{0'}_{\mathrm{X^O+H^+/X^RH}} = \frac{RT\ln 10}{F}\log\left(\frac{\gamma_{\mathrm{X^O,H^+}}\gamma_{\mathrm{H_2O}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_3O^+}}}\right) - \frac{RT\ln 10}{F}\,\mathrm{p}K_{\mathrm{X^O,H^+}}$$

the comparison between the CPET1 and CPET2 pathways is likewise governed by the following equation:

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]}{k_{\mathrm{f,C2}}^{\mathrm{H_2O}}}\right) \simeq \log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{H_2O}}[\mathrm{H_2O}]^{1/2}}{Z_{\text{mono or bi}}\chi_{\mathrm{C2}}^{\mathrm{H_2O}}}\right) + \frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^O,H^+}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_3O^+}}}\right) + \frac{\lambda_{\mathrm{C2}}^{\mathrm{H_2O}} - \lambda_{\mathrm{C1}}^{\mathrm{H_2O}}}{4RT\ln 10} - \frac{1}{2}\,\mathrm{p}K_{\mathrm{X^O,H^+}}$$

For the same reasons as before, it follows that the main governing factor is the p*K* of the ($\mathrm{X^O,H_3O^+}$) adduct.

In summary, there are thus two main possibilities for the order in which the p*K* values fall, leading to the following sequences of predominance of one pathway over the others:

$$\mathrm{p}K_{\mathrm{X^OH}} < \mathrm{p}K_{\mathrm{X^O,H^+}} < 0: \quad \text{ETPT} < \text{CPET2} < \text{CPET1}$$

$$\mathrm{p}K_{\mathrm{X^OH}} > \mathrm{p}K_{\mathrm{X^O,H^+}} > 0: \quad \text{ETPT} > \text{CPET2} > \text{CPET1}$$

In the second case there is little doubt that the stepwise ETPT pathway will surpass the CPET pathways. In the first case, the CPET pathways overcome the ETPT pathway. Such an outcome requires however that the excess driving force is sufficient to overcome the somewhat unfavorable balance of the intrinsic factors.

The equilibrium potential versus pH diagrams in Figure 2 show the zones of stabilities of the four reactants as a function of pH and potential in the two cases where $\mathrm{p}K_{\mathrm{X^OH}} < 0$ and $\mathrm{p}K_{\mathrm{X^OH}} > 0$.

In the central zone, the equilibrium redox potential varies with pH according to

$$E_{\mathrm{eq}} \simeq E^{0'}_{\mathrm{X^OH/X^RH}} - \frac{RT\ln 10}{F}(\mathrm{pH} - \mathrm{p}K_{\mathrm{X^OH}}) = E^{0'}_{\mathrm{X^O+H^+/X^RH}} - \frac{RT\ln 10}{F}\mathrm{pH}$$

(in the likely case where that the activity coefficients are close to 1).

One may of course use this pH-depending equilibrium potential to introduce an apparent driving force, $F(E_{\mathrm{eq}} - E_{\mathrm{A}})$ for the CPET1 reaction but this is not the “driving force” to be used in activation−driving force relationships describing the kinetics. The proper formal potentials to be used for defining the driving forces of the CPET1 and ETPT pathways are those indicated by the red and blue arrows, respectively.

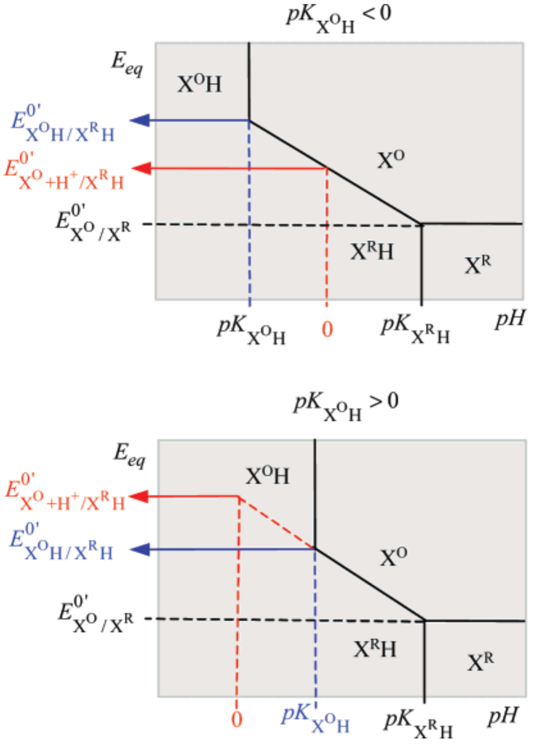

Figure 2. Equilibrium potential vs pH diagram showing the zone of stabilities of the four reactants and the formal potentials to be used in the definition of the CPET1 (red) and ETPT (blue) driving forces.

2. Two-Step and One-Step CPET OH⁻ Deprotonation Pathways. Going to higher pH values, water may be replaced by $\mathrm{OH^-}$ as proton acceptor. Here too, a two-step or a one-step process may be envisaged as depicted in Scheme 1b.

2.1. Do Driving Force and Rate Constants Depend on pH? The rate equations corresponding to the two-step reaction (CPET2 pathway in Scheme 1b) write

$$\frac{\mathrm{d}[\mathrm{X^RH,H_2O}]}{\mathrm{d}t} = -k_{-\mathrm{p}}[\mathrm{OH^-}][\mathrm{X^RH,H_2O}] + k_{\mathrm{p}}[\mathrm{H_2O}][\mathrm{X^RH,OH^-}]$$

$$\frac{\mathrm{d}[\mathrm{X^RH,OH^-}]}{\mathrm{d}t} = -k_{\mathrm{C2}}^{\mathrm{OH^-}}[\mathrm{X^RH,OH^-}] + k_{-\mathrm{C2}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}] + k_{-\mathrm{p}}[\mathrm{OH^-}][\mathrm{X^RH,H_2O}] - k_{\mathrm{p}}[\mathrm{H_2O}][\mathrm{X^RH,OH^-}]$$

$$\frac{\mathrm{d}[\mathrm{X^O,H_2O}]}{\mathrm{d}t} = k_{\mathrm{C2}}^{\mathrm{OH^-}}[\mathrm{X^RH,OH^-}] - k_{-\mathrm{C2}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}]$$

where the rate constants are as marked in Scheme 1b.

The rate constant of the second step, $k_{\mathrm{C2}}^{\mathrm{OH^-}}$ may be expressed as a combination of the activation free energy, $\Delta G_{\mathrm{C2}}^{\mathrm{OH^-}\neq}$ and of the pre-exponential factor, $Z_{\text{mono or bi}}\ \chi_{\mathrm{C2}}^{\mathrm{OH^-}}$:

$$k_{\mathrm{C2}}^{\mathrm{OH^-}} = Z_{\text{mono or bi}}\chi_{\mathrm{C2}}^{\mathrm{OH^-}}\exp\left(-\frac{\Delta G_{\mathrm{C2}}^{\mathrm{OH^-}\neq}}{RT}\right)$$

where $k_{\mathrm{C2}}^{\mathrm{OH^-}}$ and the collision factor $Z_{\text{mono or bi}}$ are monomolecular or bimolecular rate constants according to the electron acceptor being attached to the electron donor or freely diffusing in the solution. The transmission coefficient, $\chi_{\mathrm{C2}}^{\mathrm{OH^-}}$, is a measure of proton tunneling in the CPET2 reaction.

The Marcus quadratic equation may again be used to relate activation and driving force. The latter is obtained from the formal potentials of the electron acceptor, $E_{\mathrm{A}}^{0'}$ and of the second step, $E^{0'}_{\mathrm{X^O,H_2O/X^RH,OH^-}}$:

$$\Delta G_{\mathrm{C2}}^{\mathrm{OH^- 0'}} = F\left(E^{0'}_{\mathrm{X^O,H_2O/X^RH,OH^-}} - E_{\mathrm{A}}^{0'}\right)$$

where

$$FE^{0'}_{\mathrm{X^O,H_2O/X^RH,OH^-}} = \mu^{0'}_{\mathrm{X^O,H_2O}} - \mu^{0'}_{\mathrm{X^RH,OH^-}}$$

An interesting limiting situation is when formation and dissociation reactions of the OH$^-$ adduct are fast enough for the reaction to remain unconditionally at equilibrium. The kinetics then involves overall forward and backward rate constants, $k_{\mathrm{f,C2}}^{\mathrm{OH^-}}$ and $k_{\mathrm{b,C2}}^{\mathrm{OH^-}}$ defined by

$$\frac{\mathrm{d}([\mathrm{X^RH,H_2O}] + [\mathrm{X^RH,OH^-}])}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{X^O,H_2O}]}{\mathrm{d}t} = -k_{\mathrm{f,C2}}^{\mathrm{OH^-}}([\mathrm{X^RH,H_2O}] + [\mathrm{X^RH,OH^-}]) + k_{\mathrm{b,C2}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}]$$

where

$$k_{\mathrm{f,C2}}^{\mathrm{OH^-}} = \frac{\dfrac{10^{-\mathrm{p}K_{\mathrm{X^RH,H_2O}}}}{K_{\mathrm{W}}}\dfrac{\gamma_{\mathrm{X^RH,H_2O}}}{\gamma_{\mathrm{X^RH,OH^-}}}\gamma_{\mathrm{OH^-}}[\mathrm{OH^-}]}{1 + \dfrac{10^{-\mathrm{p}K_{\mathrm{X^RH,H_2O}}}}{K_{\mathrm{W}}}\dfrac{\gamma_{\mathrm{X^RH,H_2O}}}{\gamma_{\mathrm{X^RH,OH^-}}}\gamma_{\mathrm{OH^-}}[\mathrm{OH^-}]}\, k_{\mathrm{C2}}^{\mathrm{OH^-}}$$

$$k_{\mathrm{b,C2}}^{\mathrm{OH^-}} = k_{\mathrm{C-2}}^{\mathrm{OH^-}}$$

The true rate constants, $k_{\mathrm{C2}}^{\mathrm{OH^-}}$ and $k_{\mathrm{-C2}}^{\mathrm{OH^-}}$ are independent of pH as are the corresponding driving forces. The overall forward rate constant is now an increasing function of pH as a reflection of the fact that OH$^-$ is a reactant in the forward process. Conversely, the overall backward rate constant does not depend on pH.

We now lift the assumption that formation and decomposition of the OH$^-$ cluster are in unconditional equilibrium. We assume that the interaction energy within the cluster is negligible so that the coming in and out of OH$^-$ can be viewed as a diffusion process, possibly involving a Grotthuss-type mechanism. Similarly to the case of the proton expulsion mechanism, the effective rate constants are obtained from

$$-\frac{\mathrm{d}[\mathrm{X^RH,H_2O}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{X^O,H_2O}]}{\mathrm{d}t} = k_{\mathrm{f,C2}}^{\mathrm{OH^-}}[\mathrm{X^RH,H_2O}][\mathrm{OH^-}] - k_{\mathrm{b,C2}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}]$$

where

$$\frac{1}{k_{\mathrm{f,C2}}^{\mathrm{OH^-}}} = \frac{1}{k_{\mathrm{C2}}^{\mathrm{OH^-}}} + \frac{1}{k_{\mathrm{dif,OH^-}}}$$

$$\frac{1}{k_{\mathrm{b,C2}}^{\mathrm{OH^-}}} = \frac{1}{k_{\mathrm{-C2}}^{\mathrm{OH-}}} + \frac{1}{\exp\left[-\dfrac{F}{RT}\left(E_{\mathrm{A}}^{0'} - E^{0'}_{\mathrm{X^O,H_2O/X^RH,OH^-}}\right)\right]k_{\mathrm{dif,OH^-}}}$$

In the above discussion, we have considered the OH$^-$ approach and CPET from the OH$^-$ adduct thus formed as two successive steps. We now regard these two steps as concerted: the CPET reaction then includes the OH$^-$ diffusion process, even if there might be a price to pay for this in terms of reorganization energy and pre-exponential factor. The rate equation then writes as follows:

$$-\frac{\mathrm{d}[\mathrm{X^RH,H_2O}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{X^O,H_2O}]}{\mathrm{d}t} = k_{\mathrm{C1}}^{\mathrm{OH^-}}[\mathrm{X^RH,H_2O}][\mathrm{OH^-}] - k_{\mathrm{-C1}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}]$$

The driving force, defined from

$$\Delta G_{\mathrm{C1}}^{\mathrm{OH^- 0'}} = F\left(E^{0'}_{\mathrm{X^O+H_2O/X^RH+OH^-}} - E_{\mathrm{A}}^{0'}\right)$$

is governed by the formal potential

$$FE^{0'}_{\mathrm{X^O,H_2O/X^RH+OH^-}} = \mu^{0'}_{\mathrm{X^O}} + \mu^{0'}_{\mathrm{H_2O}} - \mu^{0'}_{\mathrm{X^RH}} - \mu^{0'}_{\mathrm{OH^-}}$$

The overall forward and backward rate constants, $k_{\mathrm{f,C1}}^{\mathrm{OH^-}}$ and $k_{\mathrm{b,C1}}^{\mathrm{OH^-}}$ are defined by

$$-\frac{\mathrm{d}[\mathrm{X^RH,H_2O}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{X^O,H_2O}]}{\mathrm{d}t} = k_{\mathrm{f,C1}}^{\mathrm{OH^-}}[\mathrm{X^RH,H_2O}] - k_{\mathrm{b,C1}}^{\mathrm{OH^-}}[\mathrm{X^O,H_2O}]$$

with

$$k_{\mathrm{f,C1}}^{\mathrm{OH^-}} = k_{\mathrm{C1}}^{\mathrm{OH^-}}[\mathrm{OH^-}]$$

$$k_{\mathrm{b,C1}}^{\mathrm{OH^-}} = k_{\mathrm{-C1}}^{\mathrm{OH^-}}$$

The forward rate constant may be expressed as

$$k_{\mathrm{C1}}^{\mathrm{OH^-}} = Z_{\mathrm{bi\ or\ ter}}\,\chi_{\mathrm{C1}}^{\mathrm{OH^-}}\exp\left(-\frac{\Delta G_{\mathrm{C1}}^{\mathrm{OH^-\neq}}}{RT}\right)$$

where $\Delta G_{\mathrm{C1}}^{\mathrm{OH^-\neq}}$ is the activation free energy. $k_{\mathrm{C1}}^{\mathrm{OH^-}}$ and $Z_{\mathrm{bi\ or\ ter}}$ are bimolecular or termolecular constants according to the electron acceptor being attached to the electron donor or freely diffusing in the solution. The transmission coefficient, $\chi_{\mathrm{C1}}^{\mathrm{OH^-}}$, is a measure of proton tunneling in the CPET reaction.

The rate constant of the forward reaction does not thus depend on pH, because the driving force does not depend on pH. The global rate constant of backward reaction does depend on pH, not because the second-order rate constant depends on pH but simply because the proton is a reactant in the backward reaction. The kinetics of the forward reaction depends on pH simply because OH$^-$ is a reactant, whereas the backward reaction rate constant does not depend on pH.

We may thus conclude that whether the CPET OH$^-$ deprotonation reaction involves a one-step or a two-step scenario, the overall forward rate constant depends on pH, not because its driving force depends on pH, but because OH$^-$ is a reactant in the forward process.

2.2. Competition between CPET OH$^-$ Deprotonation and Stepwise PTET Pathways. As the pH increases, possibly triggering the occurrence of the CPET OH$^-$ deprotonation pathways, the PTET stepwise pathway may also go off as the pH values come close to the pK of the reduced form of the substrate. In the case where protonation/deprotonation preceding electron transfer is at equilibrium, the kinetics of the PTET pathway (Scheme 1c) involves the overall forward and backward rate constants, k_f^X and k_b^X defined by

$$\frac{\mathrm{d}([\mathrm{X^RH}]+[\mathrm{X^R}])}{\mathrm{d}t}=-\frac{\mathrm{d}[\mathrm{X^O}]}{\mathrm{d}t}=\\ -k_\mathrm{f}^\mathrm{X}([\mathrm{X^RH}]+[\mathrm{X^R}])+k_\mathrm{b}^\mathrm{X}[\mathrm{X^O}]$$

where, by analogy with the CPET2 OH$^-$case

$$k_\mathrm{f}^\mathrm{X}=\frac{\dfrac{10^{-\mathrm{p}K_{\mathrm{X^RH}}}}{K_\mathrm{W}}\dfrac{\gamma_{\mathrm{X^RH}}}{\gamma_{\mathrm{X^R}}}\gamma_{\mathrm{OH^-}}[\mathrm{OH^-}]}{1+\dfrac{10^{-\mathrm{p}K_{\mathrm{X^RH,}}}}{K_\mathrm{W}}\dfrac{\gamma_{\mathrm{X^RH}}}{\gamma_{\mathrm{X^R}}}\gamma_{\mathrm{OH^-}}[\mathrm{OH^-}]}k_\mathrm{e}^\mathrm{X}$$

$$k_\mathrm{b}^\mathrm{X}=k_{-\mathrm{e}}^\mathrm{X}$$

We may now compare the kinetics of the three pathways at pH values where the CPET2 and PTET forward rate constants begin to be proportional to [OH$^-$]:

$$k_\mathrm{f}^\mathrm{X}=\frac{10^{-\mathrm{p}K_{\mathrm{X^RH}}}}{K_\mathrm{W}}\frac{\gamma_{\mathrm{X^RH}}}{\gamma_{\mathrm{X^R}}}\gamma_{\mathrm{OH^-}}[\mathrm{OH^-}]k_\mathrm{e}^\mathrm{X}$$

Then

$$\log\left(\frac{k_{\mathrm{f},C1}^{\mathrm{OH^-}}}{k_\mathrm{f}^\mathrm{X}}\right)=\log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{OH^-}}}{Z_{\text{mono or bi}}\kappa^\mathrm{X}}\right)+\mathrm{p}K_{\mathrm{X^RH}}+\log K_\mathrm{W}-\\ \log\left(\frac{\gamma_{\mathrm{X^RH}}}{\gamma_{\mathrm{X^R}}}\gamma_{\mathrm{OH^-}}\right)+\frac{\lambda^\mathrm{X}-\lambda_{\mathrm{C1}}^{\mathrm{OH^-}}}{4RT\ln 10}+\\ \frac{F}{RT\ln 10}\frac{E_{\mathrm{X^O/X^R}}^{0'}-E_{\mathrm{X^O+H_2O/X^R+OH^-}}^{0'}}{2}$$

$$FE_{\mathrm{X^O+H_2O/X^RH+OH^-}}^{0'}=\mu_{\mathrm{X^O}}^{0'}+\mu_{\mathrm{H_2O}}^{0'}-\mu_{\mathrm{X^RH}}^{0'}\text{ - }\mu_{\mathrm{OH^-}}^{0'}$$

and

$$FE_{\mathrm{X^O/X^R}}^{0}=\mu_{\mathrm{X^O}}^{0'}-\mu_{\mathrm{X^R}}^{0'}$$

Thus

$$E_{\mathrm{X^O/X^R}}^{0'}-E_{\mathrm{X^O+H_2O/X^RH+OH^-}}^{0'}=\\ \frac{RT\ln 10}{F}\log\left(\frac{\gamma_{\mathrm{X^RH}}\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{X^R}}\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_2O}}}\right)-\frac{RT\ln 10}{F}(\mathrm{p}K_{\mathrm{X^RH}}+\log K_\mathrm{W})$$

and

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{OH^-}}}{k_\mathrm{f}^\mathrm{X}}\right)=\log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{OH^-}}}{Z_{\text{mono or bi}}\kappa^\mathrm{X}}\right)+\frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^R}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{H_2O}}\gamma_{\mathrm{OH^-}}\gamma_{\mathrm{X^RH}}}\right)+\\ \frac{\lambda^\mathrm{X}-\lambda_{\mathrm{C1}}^{\mathrm{OH^-}}}{4RT\ln 10}+\frac{1}{2}(\mathrm{p}K_{\mathrm{X^RH}}+\log K_\mathrm{W})$$

and therefore, taking into account that $\gamma_{\mathrm{H_2O}}[\mathrm{H_2O}]=1$,

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{OH^-}}}{k_\mathrm{f}^\mathrm{X}}\right)=\log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{OH^-}}[\mathrm{H_2O}]^{1/2}}{Z_{\text{mono or bi}}\kappa^\mathrm{X}}\right)+\\ \frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^R}}}{\gamma_{\mathrm{X^O}}\gamma_{\mathrm{X^RH}}\gamma_{\mathrm{OH^-}}}\right)+\frac{\lambda^\mathrm{X}-\lambda_{\mathrm{C1}}^{\mathrm{OH^-}}}{4RT\ln 10}+\frac{1}{2}(\mathrm{p}K_{\mathrm{X^RH}}+\log K_\mathrm{W})$$

For reasons similar to those discussed before in the $\mathrm{H_3O^+/H_2O}$ case, the main factor that governs the competition between the CPET1-OH$^-$ and PTET routes is now the pK of $\mathrm{X^RH}$ being smaller or larger than $-\log K_\mathrm{W}$ (=14).

Since

$$E_{\mathrm{X^O,H_2O/X^RH,OH^-}}^{0'}-E_{\mathrm{X^O+H_2O/X^RH+OH^-}}^{0'}=\frac{RT\ln 10}{F}\cdot\\ \log\left(\frac{\gamma_{\mathrm{X^RH,OH^-}}\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{X^R}}\gamma_{\mathrm{X^O,H_2O}}\gamma_{\mathrm{H_2O}}}\right)-\frac{RT\ln 10}{F}(\mathrm{p}K_{\mathrm{X^RH,H_2O}}+\log K_\mathrm{W})$$

the comparison between the CPET1 and CPET2 pathways is likewise governed by the following equation.

$$\log\left(\frac{k_{\mathrm{f,C1}}^{\mathrm{OH^-}}}{k_{\mathrm{f,C2}}^{\mathrm{OH^-}}}\right)=\log\left(\frac{Z_{\text{bi or ter}}\chi_{\mathrm{C1}}^{\mathrm{OH^-}}[\mathrm{H_2O}]^{1/2}}{Z_{\text{mono or bi}}\chi_{\mathrm{C2}}^{\mathrm{OH^-}}}\right)+\\ \frac{1}{2}\log\left(\frac{\gamma_{\mathrm{X^R}}}{\gamma_{\mathrm{X^O,H_2O}}\gamma_{\mathrm{X^RH,OH^-}}\gamma_{\mathrm{OH^-}}}\right)+\frac{\lambda_{\mathrm{C2}}^{\mathrm{OH^-}}-\lambda_{\mathrm{C1}}^{\mathrm{OH^-}}}{4RT\ln 10}+\\ \frac{1}{2}(\mathrm{p}K_{\mathrm{X^RH,H_2O}}+\log K_\mathrm{W})$$

For the same reasons as before, it follows that the main governing factor is the pK of $\mathrm{X^RH}$ being smaller or larger than $-\log K_\mathrm{W}$ (=14).

In summary, there are thus two main possibilities for the order in which the pK values fall, leading to the following sequences of predominance of one pathway over the others.

If $\mathrm{p}K_{\mathrm{X^RH}} < \mathrm{p}K_{\mathrm{X^RH,H_2O}} < -\log K_\mathrm{W}$ (=14), the PET pathway predominates over any of the two CPET pathways. In the converse situation, $\mathrm{p}K_{\mathrm{X^RH}} > \mathrm{p}K_{\mathrm{X^RH,H_2O}} > -\log K_\mathrm{W}$ is a necessary condition for the CPET1 pathway being the most favorable. It may not be a sufficient condition. The driving force has to be sufficient to overcome the handicap deriving from a somewhat larger reorganization enegy and a somewhat smaller transmission factor.

Similarly to Figure 2, Figure 3 indicates the proper formal potentials to be used for defining the driving forces of the CPET1 and PTET pathways with red and blue arrows, respectively.

3. CPET Pathways Involving the Buffer Components. Since we selected to focus on oxidation processes, we analyze now CPET reactions that involve the basic component of the buffer, Z$^-$, as sketched in Scheme 1d. Transposition to reductions involving the acid component of the buffer is immediate.

The rate equations write

$$\frac{\mathrm{d}[\mathrm{X^RH}]}{\mathrm{d}t}=-k_\mathrm{as}^\mathrm{R}[\mathrm{Z^-}][\mathrm{X^RH}]+k_\mathrm{dis}^\mathrm{R}[\mathrm{XH^R,Z^-}]$$

$$\frac{\mathrm{d}[\mathrm{XH^R\cdots Z^-}]}{\mathrm{d}t}=-k_{\mathrm{C2}}^{\mathrm{Z^-}}[\mathrm{X^RH\cdots Z^-}]+k_{-\mathrm{C2}}^{\mathrm{Z^-}}[\mathrm{X^O\cdots HZ}]+\\ k_\mathrm{as}^\mathrm{R}[\mathrm{Z^-}][\mathrm{X^RH}]-k_\mathrm{dis}^\mathrm{R}[\mathrm{XH^R,Z^-}]$$

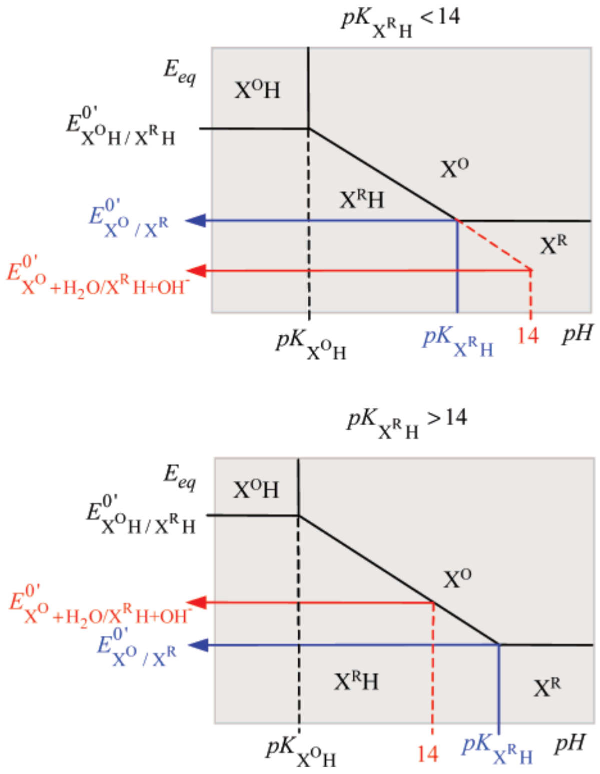

Figure 3. Equilibrium potential vs pH diagram showing the zone of stabilities of the four reactants and the formal potentials to be used in the definition of the CPET1-OH⁻ (red) and PTET (blue) driving forces.

$$\frac{\mathrm{d}[X^O\cdots HZ]}{\mathrm{d}t} = k^{Z^-}_{C2}[X^RH\cdots Z^-] - k^{Z^-}_{-C2}[X^O\cdots HZ] + k^O_{as}[HZ][X^O] - k^O_{dis}[X^O\cdots HZ]$$

$$\frac{\mathrm{d}[X^O]}{\mathrm{d}t} = -k^O_{as}[HZ][X^O] + k^O_{dis}[X^O\cdots HZ]$$

If we assume that association and dissociation of the adducts are so fast that equilibrium is unconditionally achieved, then

$$\frac{\mathrm{d}([X^RH] + [X^RH\cdots Z^-])}{\mathrm{d}t} = -\frac{\mathrm{d}([X^O] + [X^O\cdots HZ])}{\mathrm{d}t} = -k^{Z^-}_{f}([X^RH] + [X^RH\cdots Z^-]) + k^{Z^-}_{b}([X^RH] + [X^RH\cdots Z^-])$$

with (assuming that the activity coefficient of all intervening species are close to unity)

$$k^{Z-}_{f} = k^{Z^-}_{C2}\frac{K^R_{as}[Z^-]}{1 + K^R_{as}[Z^-]}$$

and

$$k^{Z^-}_{b} = k^{Z^-}_{-C2}\frac{K^O_{as}[HZ]}{1 + K^O_{as}[HZ]}$$

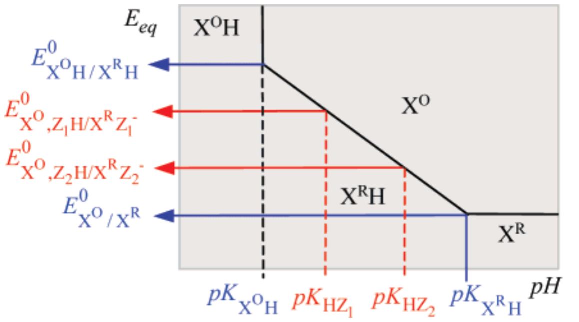

Figure 4. Standard potentials for CPET-OH⁻ pathways involving basic components of the buffer.

The forward rate constant exhibits saturation kinetics on increasing the concentration of base. A similar variation of the backward rate constant on the buffer acid concentration is expected. Focusing on oxidation, the increase of the rate constant with the base concentration is one reason for its increase with pH in experiments where pH variations around the buffer p*K* are obtained by increasing the concentration of base. When $[Z^-] \ll 1/K^R_{as}$, the variation of the rate constant with the base concentration is linear and log $k^{Z^-}_{f}$ increases proportionally to pH. The variation then tends to be less, ultimately reaching an asymptote.

The dependence of the reaction rate on the driving force can be approximated as before by

$$\Delta G^{H_2O\neq}_{C2} \simeq \frac{\lambda^{Z^-}_{C2}}{4} + F\frac{E^0_{X^O\cdots HZ/X^RH\cdots Z^-} - E^0_A}{2}$$

$$k^{Z^-}_{C2} = Z_{\text{mono or bi}}\,\chi^{Z^-}_{C2}\exp\left(-\frac{\Delta G^{Z^-\neq}_{C2}}{RT}\right)$$

$$\log(k^{Z^-}_{C2}) = \log(Z_{\text{mono or bi}}\chi^{Z^-}_{C2}) - \frac{\lambda^{Z^-}_{C2}}{4RT\ln 10} + \frac{F}{RT\ln 10}\,\frac{E^0_A - E^0_{X^O\cdots HZ/X^RH\cdots Z^-}}{2}$$

in which the standard potential of the hydrogen-bonded couple, $E^0_{X^RH\cdots Z\rightarrow X^O\cdots HZ}$, is related to the couple involving the separate reactants according to

$$E^0_{X^O\cdots HZ/X^RH\cdots Z^-} = E^0_{X^O+HZ/X^RH+Z^-} + \frac{RT\ln 10}{F}\log\left(\frac{K^R_{as}}{K^O_{as}}\right)$$

It follows that, when $[Z^-] \ll 1/K^R_{as}$,

$$\log(k^{Z^-}_{f}) = \log[Z^-] + \log(Z_{\text{mono or bi}}\chi^{Z^-}_{C2}) - \frac{\lambda^{Z^-}_{C2}}{4RT\ln 10} + \frac{1}{2}\log(K^R_{as}K^O_{as}) + \frac{F}{RT\ln 10}\,\frac{E^0_A - E^0_{X^O+HZ/X^RH+Z^-}}{2}$$

The driving force offered to the reaction is defined by the standard potential involving the separated reactants, which falls on the oblique line of the E_{eq} − pH Pourbaix diagram, as shown in Figure 4. An increase of p*K* entails an increase of the driving force offered to the reaction (as illustrated in Figure 4) and therefore a potential increase of the rate constant. Although this change in driving force is, besides [Z⁻], the second main factor of an increase of the rate constant with pH, when going from a buffer to a more basic buffer, one should also take into account that the standard rate constant (or equivalently the intrinsic barrier) and the two association constants may also vary. As to the latter factor we note that the variations of the association constants upon passing from one buffer to the other tend to compensate each other.

In all cases, the variations with pH are indirect, being caused either by an increase of the concentration of a reactant or by an increase of the buffer p*K*.

Concluding Remarks

(1) Concerted proton−electron oxidations involving water as proton acceptor may well compete favorably with electron first, proton second (ETPT) stepwise pathways. A necessary but not sufficient condition for this to happen is that the p*K* of the reduced form of the substrate is smaller than 0. This excess driving force has to be large enough for overcoming pre-exponential and reorganization factors that are somewhat unfavorable to the CPET pathways in the competition. The driving force for such CPET pathways does not vary with pH and so does the oxidation rate constant. The overall backward reaction rate constant does vary with pH, not because the driving force varies with pH, but because proton is one reactant of the backward process.

(2) In the basic pH range, concerted proton−electron oxidations involving OH^- as proton acceptor may similarly compete with proton first, electron second (PTET) stepwise pathways. The driving force of the reaction is likewise independent of pH. The overall oxidation rate constant is an increasing function of pH, not because the driving force varies with pH, but because OH^- is one reactant of the forward process. Conversely, the rate constant of the backward reaction is independent of pH. The competition between such CPET-OH^- reactions and the stepwise PTET process depends on the p*K* of the substrate being below or above 14. In the first case, the PTET pathway predominates. In the second, the CPET pathways may be the most favorable. This however requires that the excess driving force thus gained be sufficient for overcoming pre-exponential and reorganization factors that are somewhat unfavorable to the CPET pathways in the competition.

(3) When the reactions are carried out in a buffered medium, basic components of the buffer may serve as proton acceptor in a CPET mechanism. The excess driving force thus provided may make the CPET pathway predominant over the stepwise pathways. It has however to overcome unfavorable pre-exponential and reorganization factors and also possibly unfavorable values of the H-bonded association constants between the substrate and the buffer basic component.

(4) The above conclusions are based on first principles. It follows that interpretations of previous experimental data based on the incorrect notion that the driving force of CPET-H_2O reactions depends on pH [5] should be revised.

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