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On the Theory of the 'Proton Inventory' Method

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In discussing proton tunneling, the dependence of the rate constant on solvent isotopic composition has the same form as in semiclassical theory (the Gross–Butler equation) but the physical meaning of its parameters is different.

The 'proton inventory' method, *i.e.* the study of the rate constant dependence on the solvent isotopic composition, has been widely used for the elucidation of the mechanism of proton transfer reactions (for a review see, *e.g.*[1,2]). In the analysis of the data, one usually employs the notion of the coefficient of isotope partition between the solvent and the reaction transition state, *i.e.* employing a semiclassical treatment of the process. As was noted in ref. 1, an account of the proton tunneling demands a special analysis.

In this communication, we will consider the 'proton inventory' method not in the framework of the semiclassical scheme but on the basis of the quantum theory of proton transfer.[3–5] The validity of this theory, in particular for homogeneous and enzymatic hydrolysis, was shown earlier[6–9] (for a review, see ref. 5).

As in the standard theory,[1,2] we will proceed from the general expression describing the reaction rate constant k_n at the atomic fraction of deuterium n as the ratio of the sum of reaction rates of all isotopic species v_{ij} to the sum of their concentrations $[X_{ij}]$ [eqn. (1) below is written in the form corresponding to the presence of two reactive proton sites].

$$k_n = \frac{v_{HH} + v_{HD} + v_{DH} + v_{DD}}{[X_{HH}] + [X_{HD}] + [X_{DH}] + [X_{DD}]} \tag{1}$$

For each of the isotopic species, the reaction rate is proportional to its concentration, and the proportionality factor depends on the probability of proton (deuteron) tunneling, the difference of their zero energies in the initial and final states, and the energy spent against repulsion forces for the reactants approaching the optimum distance for tunneling. Hence, for each of the partial rates one can write eqn. (2),

$$v_{ij} = a_0 \kappa_{ij} \exp(-E_{ij}/RT)\,[X_{ij}] \tag{2}$$

where a_0 is the constant independent of the isotopic composition, κ is the tunneling probability, and $E_{ij} = E_{ij}(\Delta U^0) + E_{\mathrm{app}.ij}$, where $E_{ij}(\Delta U^0)$ is that part of the activation energy which depends on the zero energy difference and $E_{\mathrm{app}.ij}$ is the energy necessary for the approach of reactants.

Let us suppose that the contributions from each of the proton sites are mutually independent, *i.e.* eqns. (3).

$$\exp(-E_{ij}/RT) = \exp[-(E_i + E_j)/RT], \text{ and } \kappa_{ij} = \kappa_i \kappa_j \tag{3}$$

This relation is quite probable when one deals with two protons linked to different atoms. It seems to be much less rigid than the assumption made by the standard theory on the equal rates of decay of all transition states; this last condition may only be met in the absence of tunneling. We notice that the first of eqns. (3) does not assume that the energy is constant for one isotope at a particular site when different isotopes occupy the other site: only the equality of energy differences is substantial, *e.g.* $U^0{}_{HH} - U^0{}_{HD} = U^0{}_{DH} - U^0{}_{DD}$. From eqns. (3) we can rewrite eqn. (2) as eqn. (4),

$$v_{ij} = a_0 \gamma_i \gamma_j [X_{ij}] \tag{4}$$

denoting the product $\kappa_i \exp(-E_i/RT)$ as γ_i.

The concentration of a given isotope species is determined by the concentration of the fully protonated form X_{HH}, the deuterium atomic fraction n and the partition coefficient ϕ_i (its independence from the isotope composition of the other site is assumed), see eqns. (5).

$$[X_{DH}] = \phi_1 [X_{HH}] \left(\frac{n}{1-n}\right) \qquad [X_{HD}] = \phi_2 [X_{HH}] \left(\frac{n}{1-n}\right) \tag{5}$$
$$[X_{DD}] = \phi_1 \phi_2 [X_{HH}] \left(\frac{n}{1-n}\right)^2$$

Introducing eqns. (4) and (5) into eqn. (1), and designating $k_0 = a_0 \gamma_{1H} \gamma_{2H} [X_{HH}]$ (here γ_{iH} means γ for the proton at the ith site), we obtain eqn. (6):

$$k_n = k_0 \frac{1 + (\sigma_1 \phi_1 + \sigma_2 \phi_2)\left(\frac{n}{1-n}\right) + \sigma_1 \sigma_2 \phi_1 \phi_2 \left(\frac{n}{1-n}\right)^2}{1 + (\phi_1 + \phi_2)\left(\frac{n}{1-n}\right) + \phi_1 \phi_2 \left(\frac{n}{1-n}\right)^2} \tag{6}$$

or, in another form, eqn. (7).

$$k_n = \frac{(1 - n + \sigma_1 \phi_1)(1 - n + n\sigma_2 \phi_2)}{(1 - n + n\phi_1)(1 - n + n\phi_2)} \tag{7}$$

Here σ_i means the ratio γ_{iD}/γ_{iH}. When the number of exchangeable protons $m > 2$, eqn. (7a) results:

$$k_n = k_0 \prod^{m} (1 - n + n\sigma_i \phi_i) / \prod^{m} (1 - n + n\phi_i) \tag{7a}$$

Eqns. (7, 7a) are of a form identical to the Gross–Butler equations from standard theory which, instead of $\sigma\phi$, include ϕ^*, the partition coefficient for the transition state. For the latter state, its statistical sum is not complete, *i.e.* does not include the contribution due to movement along the reaction coordinate.

Eqn. (7) does not therefore result only from the semiclassical treatment, but is valid in the presence of a substantial tunneling contribution. The introduction of $\sigma\phi$ instead of ϕ^* has the advantage of a more general and clear physical meaning: it accounts explicitly for both the isotopic enrichment of the reactant and the difference in the transfer rates for the light and heavy isotopes (of tunneling probability and energy differences only the latter effects were included in ϕ^* in the standard theory).

Let us now consider some special consequences of eqn. (7). If the reaction involves only one proton, we obtain eqn. (8).

$$k_n = k_0(1-n+n\sigma\phi)/(1-n+n\phi) \tag{8}$$

In the absence of isotopic enrichment ($\phi = 1$), eqn. (8a) results.

$$k_n = k_0(1-n+n\sigma) \tag{8a}$$

The linear dependence of k_n upon n is usually considered as evidence for the one-proton mechanism. However, at $\phi \neq 1$ some deviation from linearity is to be expected.

For the two-proton mechanism and $\phi_1 = \phi_2 = 1$ we have eqn. (9),

$$k_n = k_0(1-n+n\sigma_1)(1-n+n\sigma_2) \tag{9}$$

i.e. a quadratic dependence. However, at $\phi_i < 1$ even in this case a practically linear function is possible[10,11] due to a compensation of kinetic (σ) and thermodynamic (ϕ) effects.

If the isotopic enrichment is absent for one of the sites but large for the other ($\phi_1 = 1$, $\phi_2 > 1$), this does not necessarily mean a marked violation of linearity. Indeed, if the kinetic effect is absent for only the second site ($\sigma_2 = 1$), eqn. (7) will take a form, eqn. (8a), at any value of ϕ_2.

Hence we can conclude that the linear dependence by itself is not an unambiguous criterion of a one- or multi-proton mechanism. For a strict analysis, we need additional data in order to obtain some independent estimates of the parameters of interest.

Finally, let us consider one further case.[1,2] At values of ϕ and $\sigma\phi$ close to 1, the corresponding sums in eqns. (7, 7a) can be considered as the main terms in the series expansion of the exponents of $n(\phi-1)$ or $n(\sigma\phi-1)$. With a large number of protons, each contributing weakly to the total isotope effect (so called 'generalized solvent effect') we have eqn. (10).

$$k_n = k_0 \exp n \sum_{1}^{m} \phi_i(\sigma_i - 1) \tag{10}$$

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