Chapter 66
Logistic vs. W–Lambert Information in Modeling Enzyme Kinetics at Quantum Level

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ABSTRACT

The logistic temporal solution of the generalized Michaelis-Menten kinetics is employed to provide a quantum basis for the tunneling time and energy evaluations of Brownian enzymic reactions. The mono-substrate and mixed inhibition cases are treated and the associated quantum diagrams of the reaction mechanisms are depicted in terms of intermediate enzyme complexes. The methodology is suited for practically controlling of the enzymic activity throughout absorption spectroscopy.

INTRODUCTION

Although in the first century from their discover the enzymes were mainly studied for elucidation of their kinetics (Schnell & Maini, 2003), emphasising on how their structure is changed with the chemical modifications of functional groups (Hirs, 1967), or for experiencing the "forced evolution" (Rigby, Burleigh, & Hartley, 1974), in current years the focus was on controlling

them towards biotechnological roles through the knowledge based methods such as the site-directed mutagenesis (Graham et al., 1994; Tyagi et al., 2005) or gene-shuffling techniques (Stemmer, 1994). However, aiming to create a better enzyme, with improved specificity near the "catalytic perfection" (Albery & Knowles, 1976), raises the intrinsic difficulty to rationalize a general model for its activity since the relatively poor level of comprehension about the enzyme machinery (Nixon, Ostermeier, & Benkovic, 1998). As such, deviations from classical behaviour were reported

for enzymes yeast alcohol dehydrogenase (Cha, Murray, & Klinman, 1989), bovine serum amine oxidase (Grant & Klinman, 1989), monoamine oxidase (Jonsson, Edmondson, & Klinman, 1994), glucose oxidation (Kohen, Jonsson, & Klinman, 1997), or for enzyme lipoxygenase (Jonsson et al., 1996), in which it was shown that H-transfer is catalysed by quantum tunneling process. These, and other experimental (Bahnson & Klinman, 1995) and computational (Bala et al., 1996; Hwang & Warshel, 1996; Alper et al., 2001; Astumian et al., 1989; Ross et al., 2003) indications of conformational fluctuations during protein dynamics, suggested the attractive hypothesis that quantum tunneling and the enzyme catalysis are inter-correlated (Ringe & Petsko, 1999; Sutcliffe & Scrutton, 2000).

The solvent dynamics, i.e. the in vitro and in vivo conditions, and "natural breathing," i.e. the quantum fluctuations in the active site, of the enzyme molecule need to be counted in a more complete picture of enzymic catalysis. However, the quantum (fluctuating) nature of the enzymic reactions can be visualised by combining the relationship between the catalytic rate (k_{cat}) and temperature (T) (DeVault & Chance, 1966) with that between the reaction rate and the turnover number or the effective time of reaction (Δt) via Heisenberg relation

$$\frac{1}{k_{cat}} \propto \Delta t \cong \frac{\hbar}{\Delta E_{tunnelling}} = \frac{\hbar}{k_B T} \qquad (1)$$

were $\hbar$ and k_B stand for the reduced Planck and Boltzmann constants, respectively. Of course, in relation (1) the equivalence between quantum statistics and quantum mechanics was physically assumed when equating the thermal and quantum (tunneling) energies, $k_B T$ and ΔE, respectively (Kleinert, Pelster, & Putz, 2002). Nevertheless, relation (1) is the basis of rethinking upon the static character of the energetic barrier, recalling the so called steady state approximation, usually

assumed in describing enzymic catalysis (Laidler, 1955), within the transition state theory (TST) (Glasstone, Laidler, & Eyring, 1941).

Basically, when applied to enzymic reactions the recent developments suggest that the "textbook" TST is, at least in some situations, necessarily flawed. This because TST primarily treat the enzymes as being only particle-like entities, completely ignoring their electronic and protonic constitution when mediate chemical information-transfer when act on substrate. On contrary, as electrical insulators the proteins can transfer their electrons only by means of wave-like properties or tunneling processes. However, while electron transfer occurs at large distances, up to ca. 25Å, the same tunneling probability may be achieved by the protium (C – H group) at the distance of 0.58Å, the specific range for enzyme-substrate binding site. Such picture is sustained also by the electrostatic complementary of the catalytic site hypothesis, first suggested by Pauling (Pauling, 1946), and then refined by Marcus theory of electron transfer in chemical reactions (Marcus, 1993), stating that the dynamic fluctuations of the environment develop the driving force for that chemical reactions proceed.

Actually, the wave-particle duality of matter allows designing new pathway from reactants (enzyme E and substrate S) to products (enzyme and product P) in a Brownian enzymic reaction (Brown, 1902)

$$E + S \leftrightarrow ES \xrightarrow{delay} EP \rightarrow E + P \qquad (2)$$
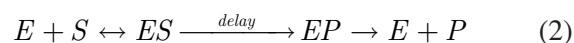
by means of passing through the barrier between the ground states of enzyme-substrate (ES) and enzyme-product (EP) complexes, employing the wave-like manifestation, instead of passing over it, as the TST predict for the particle-like manifestation of enzymes, see Figure 1. In this context, the thermal activation is realized on the basis of vibrational enhancement, at its turn sustained by quantum fluctuations of the enzyme-binding

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