

# The Intrinsic Barrier Width and its Role in Chemical Reactivity

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The Marcus dissection of activation free energy (barrier height) into the intrinsic and the thermodynamic contributions, which successfully models the interplay of rate and driving force, has led to a crucial general phenomenological consequence: the well-known two reactivity paradigms of “kinetic versus thermodynamic control”.<sup>[1]</sup> Recently, we introduced the third reactivity paradigm, quantum mechanical tunneling (QMT) control, where the reactivity is dominated by the through-the-barrier processes.<sup>[2]</sup> As a consequence, the smallest barrier width, rather than the lowest barrier height, dictates the selectivity. However, such tunneling control only describes the competition *between* through-the-barrier and over-the-barrier processes, but not reactivity and patterns *within* a set of through-the-barrier processes. Like kinetic and thermodynamic control, tunneling control is also phenomenological, whereas its conceptual origin, the Marcus dissection of barrier width,<sup>[3]</sup> i.e., the barrier-width-counterpart to the conceptual origin of kinetic and thermodynamic control, has been absent. Here we define and outline the concept of *intrinsic barrier width* and *driving force effect to the barrier width*, and report experimental as well as theoretical studies to demonstrate the distinct roles of each. We present the idea of changing the barrier widths of conformational isomerizations of some simple aromatic carboxylic acids using QMT half-lives as a readout for these changes. This allows us to draw some important conclusions about the general relevance of barrier widths, their qualitative definition, and the consequences for more complete descriptions of chemical reactions on the basis of one-dimensional reaction coordinates.

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[1] R. B. Woodward, H. Baer, *J. Am. Chem. Soc.* **1944**, *66*, 645–649.

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[3] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978.