An atom-scale model for carbon fractionation in RuBisCO

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Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) plays a pivotal role in both the Calvin and the carbon cycles. Its global significance is observed through the isotopic composition of carbon reservoirs, as the atmosphere is enriched in ^{13}C while the biosphere is more enriched in ^{12}C due to RuBisCO preferentially adding light carbon. Changes in relative abundances of carbon isotopes are signals of life in the geologic record that are linked to eras of ecological abundance and mass extinction. However, experimentally observed variations in carbon fractionation across species would influence this signal during times of evolutionary diversification. Understanding the origin of these species-wide variations requires a refined mechanism for carbon fractionation by the RuBisCO enzyme. Using potential energy surfaces from electronic structure calculations on simplified models of the active site, we estimate rate and equilibrium constants for ^{12}C and ^{13}C addition in RuBisCO. We see that the observed biological fractionation values can be constrained between a model of irreversible carbon addition and a model of equilibrium carbon addition (Figure 1). We propose that RuBisCO enzymes switch between these two modes of carbon addition, challenging models of CO_2 addition via a pre-equilibrium mechanism.

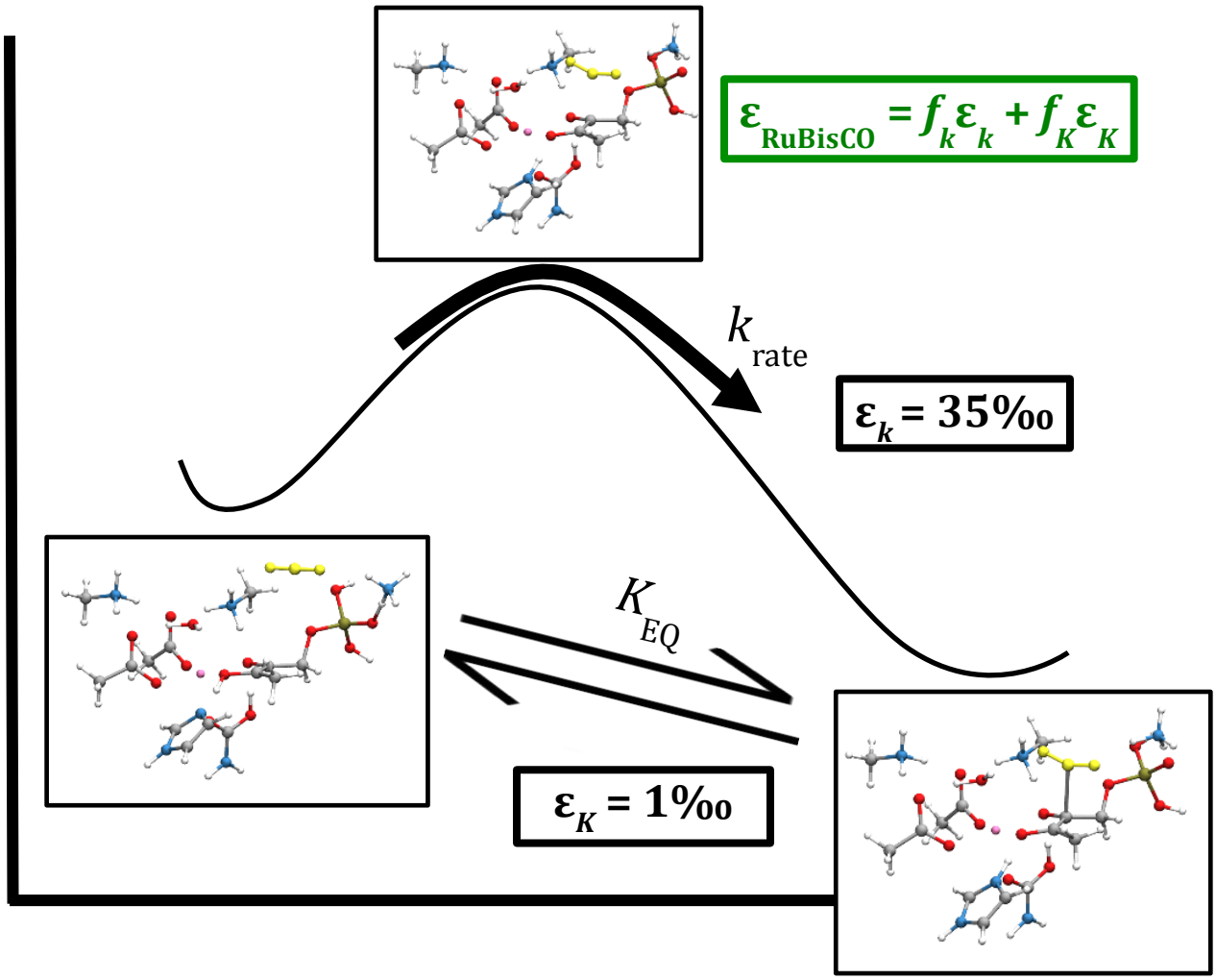

Figure 1. Calculated fractionation values assuming irreversible CO_2 addition, ε_k=35‰, and CO_2 addition via an equilibrium process, ε_K=1‰, span the *in vitro* RubisCO fractionation data. Fractionation due to a RuBisCO enzyme, $\varepsilon_{RubisCO}$, is proposed to be a linear combination of the fraction of the time that the active site allows carboxylation via an irreversible, f_k, or equibrium, f_K, process.