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Supporting Information

The Interplay of Thermodynamics and Kinetics
in Dictating Organocatalytic Reactivity and Selectivity

Kinetic Modeling

Kinetic modeling is carried out using Copasi 4.6 (Build 32). COPASI is a simulator for biochemical networks. It is a joint project by the Mendes group (VBI and University of Manchester) and the Kummer group (University of Heidelberg).

See: www.copasi.org and: Hoops, S.; Sahle, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer, U. *Bioinformatics* **2006**, *22*, 3067.

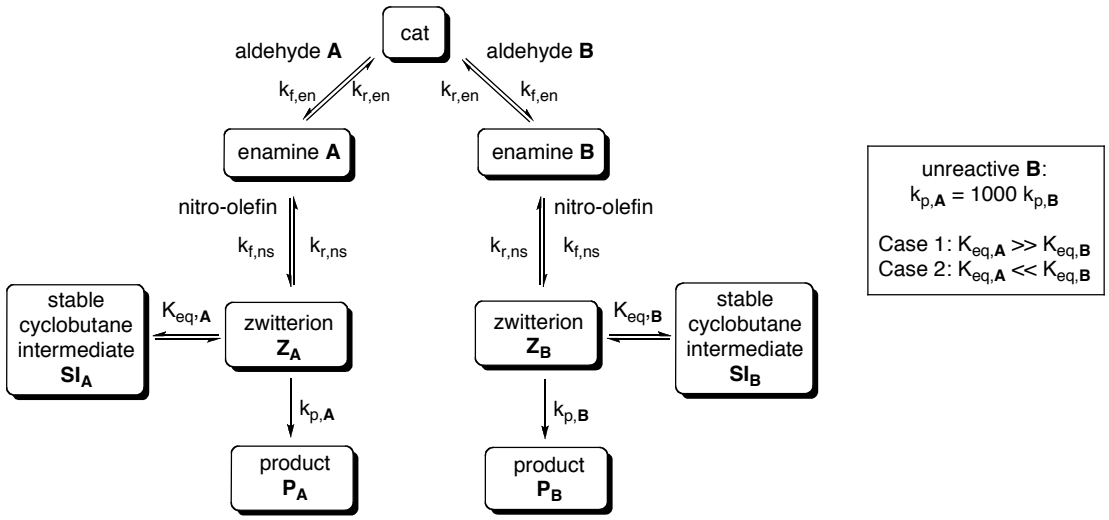
1. Stoichiometric reaction model of Scheme 6 (Figures 1 and 2).

$$en + no \underset{k_{SM}}{\overset{k_{f,en}}{\rightleftharpoons}} \mathbf{Z} \qquad K_{eq,en} = \frac{k_f}{k_{SM}} = 1\ \mathrm{M}^{-1} \qquad [en]_0 = [no]_0 = 100$$

$$\mathbf{Z} \underset{k_r}{\overset{k_{SI}}{\rightleftharpoons}} \mathbf{SI} \qquad K_{eq} = \frac{k_{SI}}{k_r} = 1000 \qquad k_{SI} = k_{SM}$$

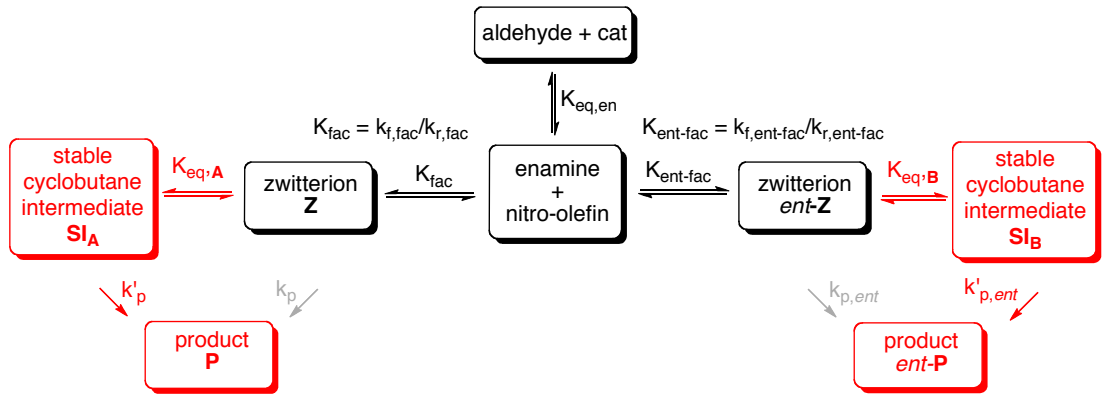
$$\mathbf{Z} \xrightarrow{k_p} \mathbf{P} \qquad 10^{-6} k_{SI} \le k_p \le 10 k_{SI}$$

2. Competitive aldehyde reaction model of Scheme 7 (Figure 3).



	Values[kfen]	Values[kren]	Values[kfns]	Values[krns]	Values[KeqA]	Values[KeqB]	Values[kp,A]	Values[kp,B]
Case 1, Scheme 7	1000	1000	1000	1000	1000	1	1	0.001
Case 2, Scheme 7	1000	1000	1000	1000	1	1000	1	0.001

3. Simulations for Scheme 10 and Figure 4.



off-cycle cyclobutanes (grey) pathways	
Figure 4a	Figure 4b
$k_p = k_{p,ent}$	$k_p = 10\ k_{p,ent}$
Case 1: $K_{eq,A} >> K_{eq,B}$	Case 3: $K_{eq,A} >> K_{eq,B}$
Case 2: $K_{eq,B} >> K_{eq,A}$	Case 4: $K_{eq,B} >> K_{eq,A}$

on-cycle cyclobutanes (red) pathways	
Figure 5a	Figure 5b
$k'_p = k'_{p,ent}$	$k'_p = 10\ k'_{p,ent}$
Case 1': $K_{eq,A} >> K_{eq,B}$	Case 3': $K_{eq,A} >> K_{eq,B}$
Case 2': $K_{eq,B} >> K_{eq,A}$	Case 4': $K_{eq,B} >> K_{eq,A}$

Figure 4:
blue bars: $K_{eq,A} = 1000$; $K_{eq,B} = 1$
pink bars: $K_{eq,B} = 1000$; $K_{eq,A} = 1$

Fig. 4 facial selectivity:

1:1	$k_{f,fac}/k_{f,ent\text{-}fac} = 1:1$
2:1	$k_{f,fac}/k_{f,ent\text{-}fac} = 2:1$
5:1	$k_{f,fac}/k_{f,ent\text{-}fac} = 5:1$
10:1	$k_{f,fac}/k_{f,ent\text{-}fac} = 10:1$

for all cases:
$k_{r,fac} = k_{r,ent\text{-}fac}$