A Thermodynamic and Kinetic Analysis of Solvent-enhanced Selectivity in Monophasic and Biphasic Reactor Systems

Supporting Information

T.J. Schwartz^{a,*} and J.Q. Bond^{b,*}

^aChemical & Biological Engineering, University of Maine, Orono, ME 04469. ^bBiomedical & Chemical Engineering, Syracuse University, Syracuse, NY 13244. ^{*}Corresponding authors thomas.schwartz@maine.edu and jqbond@syr.edu

To derive a rate expression for a reaction in solution, we begin with the fundamental rate expression for an elementary step according to Transition State Theory (TST):

$$r_i = \nu_i^{\dagger} \cdot \left[TS_i^{\dagger} \right] \tag{1}$$

Subsequently, we invoke the assumption that the transition state exists in equilibrium with the reacting species that form it. This allows one to develop the transition state concentration as a function of the equilibrium constant, K_i^{\ddagger} , which reflects the free energy change incurred by forming the transition state from the reactants, i.e., the free energy of activation.

$$K_i^{\ddagger} = \prod_j a_j^{\nu_j} \tag{2}$$

Working with a pure species reference state, thermodynamic activities are expressed as the product of species activity coefficients and species mole fractions, which are expressed as the mole numbers for species j (N_j) divided by the total moles in the system (N):

$$a_j = \gamma_j \cdot x_j \tag{3}$$

This convention applies for transition states and reactants alike; hence, the transition state concentration (the molar quantity of the transition state divided by the system volume, V) can be developed as a function of thermodynamic activities for reacting species and the activity coefficient for the transition state:

$$\left[TS_i^{\dagger}\right] = K_i^{\dagger} \cdot \frac{1}{\gamma_{TS_i}} \cdot \prod_{j=Reactants} a_j^{\nu_j} \cdot \frac{N}{V}$$

$$\tag{4}$$

Substituting this result into the TST rate expression yields:

$$r_i = \nu_i^{\ddagger} \cdot K_i^{\ddagger} \cdot \frac{1}{\gamma_{TS_i}} \cdot \prod_{j=Reactants} a_j^{\nu_j} \cdot \frac{N}{V}$$
(5)

In Transition State Theory, one assumes that the equilibrium constant, K_i^{\ddagger} can be expressed as the product of a single, low frequency vibrational mode and the standard state free energy of forming the transition state from the reactants:

$$K_i^{\ddagger} = \frac{k_B T}{h\nu_i^{\ddagger}} \cdot e^{\left(\frac{-\Delta G_i^{\circ,\ddagger}}{RT}\right)} \tag{6}$$

In Equation 6, the indicated free energy transition represents the standard state free energy change of forming the transition state as a pure species from the reactants as pure species. It is thus independent of solvent identity. Substituting this expression into equation 5 gives the expected result for the rate of an elementary step in a thermodynamically non-ideal liquid phase:

$$r_i = \frac{k_B T}{h} \cdot e^{\left(\frac{-\Delta G_i^{\circ, \ddagger}}{RT}\right)} \cdot \frac{1}{\gamma_{TS_i}} \cdot \prod_{j=Reactants} a_j^{\nu_j} \cdot \frac{N}{V}$$
(7)

The product of the frequency factor and the standard state free energy of activation is lumped hereafter in our analysis as a standard state rate constant:

$$k_i^{\circ} = \frac{k_B T}{h} \cdot e^{\left(\frac{-\Delta G_i^{\circ,\dagger}}{RT}\right)} \tag{8}$$

For the simplified analysis presented in the article, we have assumed two-step mechanisms for both sugar dehydration and furan degradation. Further, we have assumed that the second step-the step involving protonated intermediates-controls the rate of reaction for both pathways.

The rate for step 2 in each pathway is given by equations 7 and 8 such that:

$$r_A = k_{2A}^{\circ} \cdot \frac{1}{\gamma_{TS_{2A}}} \cdot a_{I_A} \cdot \frac{N}{V}$$

$$\tag{9}$$

$$r_B = k_{2B}^{\circ} \cdot \frac{1}{\gamma_{TS_{2B}}} \cdot a_{I_B} \cdot \frac{N}{V}$$

$$\tag{10}$$

Relative to this step, we assume that protonation is rapid and quasi-equilibrated. Accordingly, one can derive the thermodynamic activity of the protonated intermediate, a_{I_i} , as a function of proton activity, stable reactant activity, and equilibrium constants for protonation, K_{1A}° and K_{1B}° .

$$a_{I_A} = K_{1A}^{\circ} \cdot a_A \cdot a_{H^+} \tag{11}$$

$$a_{I_B} = K_{1B}^{\circ} \cdot a_B \cdot a_{H^+} \tag{12}$$

To faciliate a concise and simple analysis, we assume that the free proton concentration is always approximately equal to the total proton concentration. Combining Equations 9 - 12 results in the overall rate expressions for each pathway presented in the main article.

$$r_A = k_{2A}^{\circ} \cdot K_{1A}^{\circ} \cdot \frac{1}{\gamma_{TS_{2A}}} \cdot a_A \cdot a_{H^+} \cdot \frac{N}{V}$$

$$\tag{13}$$

$$r_B = k_{2B}^{\circ} \cdot K_{1B}^{\circ} \cdot \frac{1}{\gamma_{TS_{2B}}} \cdot a_B \cdot a_{H^+} \cdot \frac{N}{V}$$
(14)

We have defined an instantaneous selectivity as the net rate of furan formation (species B) divided by the net rate of degradation product formation (species C):

$$S_B = \frac{r_A - r_B}{r_B} \tag{15}$$

Substituting overall rate expressions from Equations 13 and 14, along with the activity definition given in Equation 3, into Equation 15, one generates the selectivity expression presented in the article:

$$S_B = \left(\frac{k_{2A}^{\circ} \cdot K_{1A}^{\circ} \cdot x_A}{k_{2B}^{\circ} \cdot K_{1B}^{\circ} \cdot x_B}\right) \left(\frac{\gamma_{TS_{2B}} \cdot \gamma_A}{\gamma_{TS_{2A}} \cdot \gamma_B}\right) - 1$$
(16)

To develop the analogous expression for a biphasic reactor, we redefine the instantaneous selectivity toward the furan in terms of extensive formation and consumption rates for each species in each phase. We have assumed phase equilibrium, which implies an equal and non-zero chemical potential of sugars (A), furans (B), and protons (H⁺) in each phase. Therefore, we allow for the possibility that all reactions can occur in all phases, and we scale intensive rates (Equations 13 and 14) by the volumes of the aqueous (V_{AQ}) and organic (V_{OR}) phases.

$$S_{B} = \frac{r_{A,AQ} \cdot V_{AQ} + r_{A,OR} \cdot V_{OR} - r_{B,AQ} \cdot V_{AQ} - r_{B,OR} \cdot V_{OR}}{r_{B,AQ} \cdot V_{AQ} + r_{B,OR} \cdot V_{OR}}$$
(17)

Substitution of rate expressions and thermodynamic activity definitions proceeds as described in developing the selectivity expression for the monophasic reactor (Equation 16). We additionally express organic species mole fractions as functions of aqueous species mole fractions. This calculation is based on the notion that there is a fixed total quantity of species A and species B, and they are distributed between aqueous and organic phases:

$$N_{j} = N_{j,AQ} + N_{j,OR} = x_{j,AQ} \cdot N_{AQ} + x_{j,OR} \cdot N_{OR}$$
(18)

Since we have assumed phase equilibrium, each species has equal chemical potential and equal thermodynamic activity in each phase:

$$\gamma_{j,AQ} \cdot x_{j,AQ} = \gamma_{j,OR} \cdot x_{j,OR} \tag{19}$$

Subsequently, one can develop the following expressions for the aqueous phase mole fraction of component A and of component B:

$$x_{A,AQ} = \frac{N_A}{N_{AQ} + \frac{\gamma_{A,AQ}}{\gamma_{A,OR}} \cdot N_{OR}}$$
(20)

$$x_{B,AQ} = \frac{N_B}{N_{AQ} + \frac{\gamma_{B,AQ}}{\gamma_{B,OR}} \cdot N_{OR}}$$
(21)

Moving forward, we consider that the total molar quantities of A and B in the system are small relative to solvent quantities and that there is no solvent exchange between the two phases. Accordingly, the total number of moles in the aqueous phase is approximately equal to the moles of water in the system, and the total number of moles in the organic phase is approximately equal to the moles of solvent in the system. Making appropriate substitutions into equation 17 gives the selectivity expression for the biphasic reactor.

$$S_B = \left(\frac{k_{2A}^{\circ} \cdot K_{1A}^{\circ} \cdot N_A \cdot \gamma_{A,AQ} \cdot \gamma_{TS_{2B},AQ}}{k_{2B}^{\circ} \cdot K_{1B}^{\circ} \cdot N_B \cdot \gamma_{B,AQ} \cdot \gamma_{TS_{2A},AQ}}\right) \left(\frac{1 + \frac{\gamma_{B,AQ} \cdot N_{OR}}{\gamma_{B,OR} \cdot N_{AQ}}}{1 + \frac{\gamma_{A,AQ} \cdot N_{OR}}{\gamma_{A,OR} \cdot N_{AQ}}}\right) \left(\frac{1 + \frac{\gamma_{TS_{2A},AQ} \cdot N_{OR}}{\gamma_{TS_{2B},OR} \cdot N_{AQ}}}{1 + \frac{\gamma_{TS_{2B},AQ} \cdot N_{OR}}{\gamma_{TS_{2B},OR} \cdot N_{AQ}}}\right) - 1 \quad (22)$$

In the final manuscript, we have lumped rate and equilibrium constants:

$$k^{\circ} = \frac{k_{2A}^{\circ} \cdot K_{1A}^{\circ}}{k_{2B}^{\circ} \cdot K_{1B}^{\circ}} \tag{23}$$