

Electronic Supplementary Information

Disentangling reaction rate acceleration in water microdroplets

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Theory of rate acceleration factors (RAFTs) in water microdroplets

The rate acceleration factor (RAF) is defined as (see Ref. 10 of the manuscript):

$$RAF = \frac{k_{microdroplet}}{k_{bulk}} \quad (1)$$

where $k_{microdroplet}$ is the effective rate constant observed in microdroplet experiments and k_{bulk} the corresponding property in bulk water solution at the same temperature. Since many factors can affect the value of $k_{microdroplet}$ (ionic strength, composition, droplet size, diffusion coefficients, electric fields, solvent evaporation,...), a full theoretical description of this property is extremely complex. The purpose here is to establish a set of useful kinetic equations describing the behavior of an ideal system that meets certain predefined criteria and allows rationalizing the experimental measurements. Deviation from this ideal behavior can then be taken into account by adding specific corrections for the real system. The model used in this work is described in Fig. 1 of the main text of the manuscript.

For the sake of clarity, let us first assume the following non-reversible monomolecular reaction going through transition state TS:



If the number of moles of species A at the interface and interior layers are n_s^A and n_i^A , respectively, the equilibrium hypothesis reads:

$$K_{si}^A = \frac{[A]_s}{[A]_i} = \frac{n_s^A/V_s}{n_i^A/V_i} \quad (3)$$

where K_{si}^A is the partition constant for species A. It follows:

$$n_s^A = n_i^A K_{si}^A \frac{V_s}{V_i} \quad (4)$$

The partition constant can be obtained from calculated free energy profiles of adsorption or by different experimental techniques. As will appear below, a key relationship is the ratio between the global concentration in the microdroplet $[A] = (n_s^A + n_i^A)/V$ and the concentration in the microdroplet interior, $[A]_i = n_i^A/V_i$. Simple algebra leads to:

$$\frac{[A]}{[A]_i} = 1 + \frac{V_s}{V} (K_{si}^A - 1) \quad (5)$$

Similar expressions can be written for the TS partition constant K_{si}^{TS} and TS concentration.

Under the equilibrium hypothesis, the partition constants K_{si}^{TS} and K_{si}^A are related to the kinetic constants at the surface and in the interior of the microdroplet by the equation:

$$K_{si}^{TS} = \frac{k_s}{k_i} K_{si}^A \quad (6)$$

This equality is easily obtained after substituting the different constants by their expressions in terms of free energies at temperature T in the two layers using TST, namely:

$$K_{si}^{TS} = e^{-\frac{\Delta G_{si}^{TS}}{RT}} \quad (7)$$

$$K_{si}^A = e^{-\frac{\Delta G_{si}^A}{RT}} \quad (8)$$

$$k_s = \frac{k_b T}{h} e^{-\frac{\Delta G_s^\ddagger}{RT}} \quad (9)$$

$$k_i = \frac{k_b T}{h} e^{-\frac{\Delta G_i^\ddagger}{RT}} \quad (10)$$

where k_b is Boltzmann constant, h is Planck constant, R is the ideal gas constant, T is the temperature, $\Delta G_{si}^{TS} = G_s^{TS} - G_i^{TS}$, $\Delta G_{si}^A = G_s^A - G_i^A$, and the activation free energies are $\Delta G_s^\ddagger = G_s^{TS} - G_s^A$ and $\Delta G_i^\ddagger = G_i^{TS} - G_i^A$.

Note that equation (6) can also be written as:

$$K_{si}^{TS} = \frac{k_s [A]_s}{k_i [A]_i} \quad (11)$$

which highlights the fact that the only condition for the reaction rate at the microdroplet surface ($k_s [A]_s$) to be larger than in the interior ($k_i [A]_i$) is that the TS displays some interface affinity ($K_{si}^{TS} > 1$). Because affinity for the air-water interface proves to be a quite general molecular property, this condition is arguably an important factor explaining the acceleration of reaction rates in water microdroplets. However, as we show now, the relationship between surface and microdroplet rates is a bit more intricate.

The rate equation for the whole microdroplet:

$$\frac{d[P]}{dt} = k_{microdroplet} [A] \quad (12)$$

must account for the reactions at the surface and the interior, which assuming a non-saturated system can be written:

$$\begin{aligned} \frac{d[P]}{dt} &= -\frac{d[A]}{dt} = -\frac{1}{V}\left(\frac{dn_s^A}{dt} + \frac{dn_i^A}{dt}\right) = \frac{1}{V}(k_s n_s^A + k_i n_i^A) = \frac{1}{V}\left(k_s K_{si}^A \frac{V_s}{V_i} + k_i\right) n_i^A = \left(k_s K_{si}^A \frac{V_s}{V} + k_i \frac{V_i}{V}\right) [A]_i \\ &= \frac{k_s K_{si}^A \frac{V_s}{V} + k_i \frac{V_i}{V}}{\left(1 + \frac{V_s}{V}(K_{si}^A - 1)\right)} [A] \end{aligned} \quad (13)$$

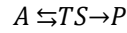
Using the equality $\frac{V_i}{V} = \left(1 - \frac{V_s}{V}\right)$ and equation (11) for K_{si}^{TS} , one gets the following expression for the global microscale rate constant:

$$k_{microdroplet} = \frac{1 + \frac{V_s}{V}(K_{si}^{TS} - 1)}{1 + \frac{V_s}{V}(K_{si}^A - 1)} k_i \quad (14)$$

and since $k_i \simeq k_{bulk}$, the expression for RAF becomes:

$$RAF = \frac{\left(1 + \frac{V_s}{V}(K_{si}^{TS} - 1)\right)}{\left(1 + \frac{V_s}{V}(K_{si}^A - 1)\right)} \quad (15)$$

monomolecular reaction



The development for more complex reactions follows similar steps. For instance, for the bimolecular reaction:



the relevant equations are:

$$\frac{d[P]}{dt} = k_{microdroplet} [A][B] \quad (17)$$

$$\frac{d[P]}{dt} = \left(k_s K_{si}^A K_{si}^B \frac{V_s}{V} + k_i \frac{V_i}{V}\right) [A]_i [B]_i \quad (18)$$

$$K_{si}^{TS} = \frac{k_s}{k_i} K_{si}^A K_{si}^B \quad (19)$$

$$k_{microscale} = \frac{\left(1 + \frac{V_s}{V}(K_{si}^{TS} - 1)\right)}{\left(1 + \frac{V_s}{V}(K_{si}^A - 1)\right)\left(1 + \frac{V_s}{V}(K_{si}^B - 1)\right)} k_i \quad (20)$$

$$RAF = \frac{\left(1 + \frac{V_s}{V}(K_{si}^{TS} - 1)\right)}{\left(1 + \frac{V_s}{V}(K_{si}^A - 1)\right)\left(1 + \frac{V_s}{V}(K_{si}^B - 1)\right)} \quad (21)$$

bimolecular reaction $A + B \rightleftharpoons TS \rightarrow P$

And for the general reaction:



$$\frac{d[P]}{dt} = k_{microdroplet} [A]^a [B]^b [C]^c \dots \quad (23)$$

$$RAF = \frac{\left[1 + \frac{V_s}{V}(K_{si}^{TS} - 1)\right]}{\left[1 + \frac{V_s}{V}(K_{si}^A - 1)\right]^a \left[1 + \frac{V_s}{V}(K_{si}^B - 1)\right]^b \left[1 + \frac{V_s}{V}(K_{si}^C - 1)\right]^c \dots} \quad (24)$$

general reaction $aA + bB + cC + \dots \rightleftharpoons TS \rightarrow P$

Since in most interesting cases the diameter of the microdroplet D is much larger than the interface thickness t , in the preceding equations one can use the following first-order approximation:

$$\frac{V_s}{V} \simeq \frac{6t}{D} \quad (25)$$

The interface thickness t is not a well-defined parameter but can be estimated theoretically by the analysis of density profiles. In a pure water droplet, it is typically related to the thickness corresponding to a change of the water density from 90% to 10%, although this property can change significantly depending on the adsorbed solute size and properties. Molecular dynamics simulations of various species at the air-water interface (see for instance Ref. 11) have shown that t falls in the nanometric scale, as is typically close to 1 nm. Hence, in this work, for microdroplets of diameter $8\mu\text{m}$ we have simply taken $\frac{V_s}{V} = 0.001$ (leading to $t=1.3$ nm). Calculated RAF values change a little by changing this coefficient but are not excessively sensitive to it.

The variation of RAF as a function of partition and rate constants has been illustrated in the manuscript for two cases, the monomolecular reaction $A \rightarrow P$ and the second-order reaction $2A \rightarrow P$. Fig. S1 displays some results for a more general bimolecular reaction $A + B \rightarrow P$. It compares the predicted values of RAF as a function of the reactants partition constants, kinetic constants and microdroplet dimensions. Fig. S2, on the other hand, displays the

behavior of the $1 + \frac{V_s}{V}(K_{si}^X - 1)$ terms appearing in RAF expressions. The terms remain close to 1 until the partition constant K_{si}^X becomes close to $\frac{V}{V_s}$, then they increase rapidly.

Calculation of partition constants

The partition constants of the reactants shown in Scheme 1 of the manuscript were calculated as follows. The COSMOtherm program¹ was used using the Flatsurf option and the parameter file BP_TZVPD_FINE_C30_1601.ctd to obtain the free energy gain in going from bulk water to the vacuum-liquid water interface. We did not account for conformational average

because due to the great number of degrees of freedom and flexibility of the diamino compound, such calculation would require a detailed conformational study using for instance molecular dynamics. Therefore, we decided to use the maximum gain provided by the program (G_{min}). The calculated free energies at 300K were $-3.05 \text{ kcal}\cdot\text{mol}^{-1}$ and $-4.53 \text{ kcal}\cdot\text{mol}^{-1}$ for propenamide (**1**) and N',N'-dibutylpropane-1,3-diamine (**2**), respectively. The corresponding partition constants are $K_{si}^{(1)} = 1.7 \cdot 10^2$ and $K_{si}^{(2)} = 2.0 \cdot 10^3$.

¹ COSMOtherm, Version C3.0, Release 17.01; COSMOlogic GmbH & Co. KG, <http://www.cosmologic.de>; Eckert, F. and A. Klamt, *AIChE Journal*, 48, 369 (2002).

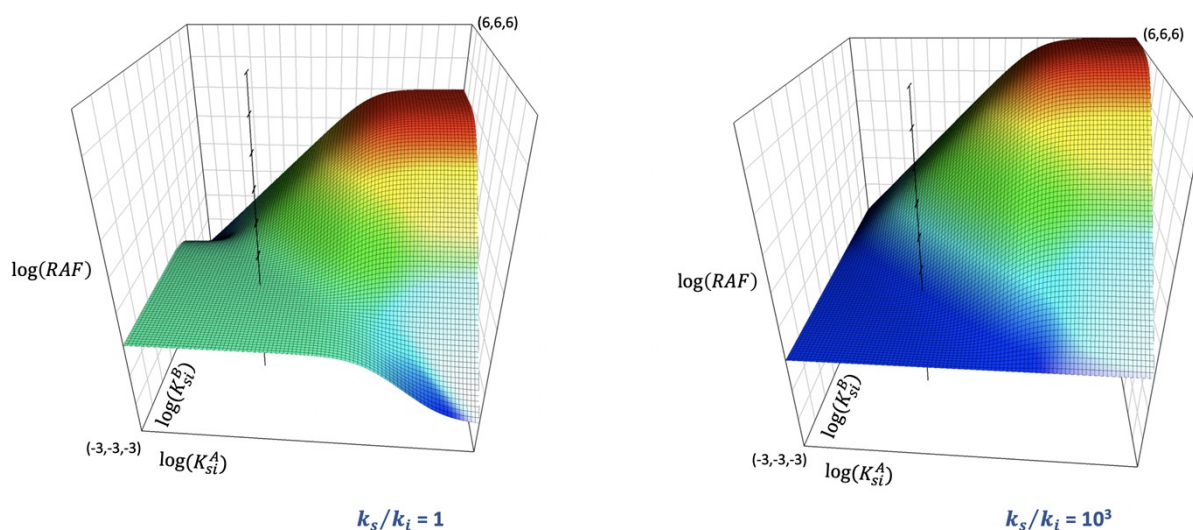


Fig. S1. Examples of variation of $\log(\text{RAF})$ for a second-order reaction $A + B \rightarrow P$ in a water microdroplet as a function of $\log(K_{si}^A)$ and $\log(K_{si}^B)$. The surfaces correspond to a

microdroplet with a volume ratio $V_s/V = 10^{-3}$ and compare the results for two different values of k_s/k_i . The limits of the (x,y,z) plots are indicated.

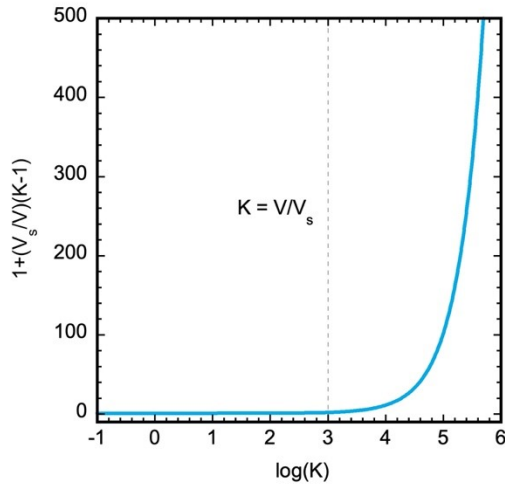


Fig. S2. Shape of the function $1 + \frac{V_s}{V}(K - 1)$ in a logarithmic scale. This function represents the ratio between the global concentration of a given species in the microdroplet and in the microdroplet interior. We assume a microdroplet volume ratio $V_s/V = 10^{-3}$.