SUPPORTING INFORMATION

A Classic, Azo-Dye Agglomeration System: Evidence for Slow, Continuous Nucleation, Autocatalytic Agglomerative Growth, Plus the Effects of Dust-Removal by Microfiltration on the Kinetics

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S1 Derivation of the Kinetic Equations Employed in the Main Text

The kinetics derivation which follows refers back to Scheme 3 of the main text. The relevant kinetic equations, derived based on the mechanism provided in Scheme 3, are the following:

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{1/n}\frac{d[B_n]}{dt} = k_1[A] + k_2[A][B] \tag{S1}$$

Since the concentration of water does practically not change during the reaction the constant $[H_2O]$ is absorbed into the apparent rate constants k_1 and k_2.

What is actually monitored is the absorbance at 475 nm, A_{475}, assigned in the original 1978 publication[1] to the agglomerated dye, B_n. By Beer's law we can write the following equations:

What we need are expressions for $[A]_t$, $[B]_t$, and $[B]_\infty$ in terms of A_{475} measurable.

$A_{475} = \varepsilon_{475}\, b\, [B_n]$, but since $[B] = \frac{1}{n}[B_n]$, that is, $[B_n] = n\,[B]$ $\tag{S2a}$

$A_{475} = \varepsilon_{475}\, b\, n[B]$, or $\tag{S2b}$

$$[B]_t = \frac{1}{nb\varepsilon_{475}}(A_{475})_t \tag{S2c}$$

and since $n[B]_\infty = [B_n]_\infty$ and for a reaction with single product by mass balance in eq 5 of Scheme 3 in the main text, $[B]_\infty = [A]_o$

$$[A]_o = [B]_\infty = \frac{1}{nb\varepsilon_{475}}(A_{475})_\infty \tag{S2d}$$

Next we need expressions for $[A]_o$ and $[A]_t$ in terms of A_{475} measurable. Our mass balance and initial reactant, $[A]_o$, vs final product, $[B]_\infty$, equations give us the needed results:

$[A]_o = [A]_t + [B]_t$ $\tag{S3a}$

$[A]_o = [B]_\infty$ so $\tag{S3b}$

$$[A]_t = [B]_\infty - [B]_t \tag{S3c}$$

Now combining eqs (S8c), (S7c) and (S7d) yields eq (S4):

$$[A]_t = \frac{1}{nb\varepsilon_{475}} ((A_{475})_\infty - (A_{475})_t) \tag{S4}$$

We can now combine eq (S4) with eq (S1) to yield eqs (S5)

$$\frac{d[B]}{dt} = \frac{1}{nb\varepsilon_{475}} \frac{d(A_{475})}{dt} = \frac{1}{nb\varepsilon_{475}} k_1[(A_{475})_\infty - (A_{475})_t] + \left(\frac{1}{nb\varepsilon_{475}}\right)^2 k_2(A_{475})_t[(A_{475})_\infty - (A_{475})_t] \tag{S5a}$$

Eq (S5a) simplifies to eq (S5b) by substituting (A_{475}) for $(A_{475})_t$

$$\frac{d(A_{475})}{dt} = k_1[(A_{475})_\infty - (A_{475})] + \frac{1}{nb\varepsilon_{475}} k_2(A_{475})_t[(A_{475})_\infty - (A_{475})] \tag{S5b}$$

or to eq (S5c) by substituting $k_2' = k_2/nb\varepsilon_{475}$

$$\frac{d(A_{475})}{dt} = k_1[(A_{475})_\infty - (A_{475})] + k_2'(A_{475})_t[(A_{475})_\infty - (A_{475})] \tag{S5c}$$

$$\text{where } k_2' = k_2 \left(\frac{1}{nb\varepsilon_{475}}\right) = k_2 \frac{1}{C_1}$$

$$C_1 = constant = nb\varepsilon_{475} \text{ or } k_2 = (nb\varepsilon_{475}) k_2' = C_1 k_2'$$

Eq (S5c) looks exactly like the $\frac{d[B]}{dt}$ form of eq (S1), repeated below, for which the integrated rate equation is eq (S6)

$$\frac{d[B]}{dt} = k_1[A] + k_2[A][B] \tag{S1}$$

$$[B]_t = [A]_o \left(1 - \frac{k_1 + k_2[A]_o}{k_2[A]_o + k_1 e^{(k_1 + k_2[A]_o)t}}\right) \tag{S6}$$

By analogy, the integrated rate equation for eq (S5b) is given eqs (S7a), (S7b), (S7c), and (S8):

$$[B]_t = \left(\frac{1}{nb\varepsilon_{475}}\right)(A_{475})_t = \frac{1}{C_1}(A_{475})_t \tag{S7a}$$

$$[A]_t = \frac{1}{nb\varepsilon_{475}}\left((A_{475})_\infty - (A_{475})_t\right) = \frac{1}{C_1}\left((A_{475})_\infty - (A_{475})_t\right) \tag{S7b}$$

$$[A]_o = [B]_\infty = \frac{1}{nb\varepsilon_{475}}(A_{475})_\infty = \frac{1}{C_1}(A_{475})_\infty \tag{S7c}$$

The integration of eq (S5c) yields eq (S8):

$$(A_{475})_t = (A_{475})_\infty \left(1 - \frac{k_1 + k_2'(A_{475})_\infty}{k_2'(A_{475})_\infty + k_1 e^{(k_1 + k_2'(A_{475})_\infty)t}}\right) \tag{S8}$$

Comparing of eq (S8) to eq (S6) reveals that using the integrated rate equation (S8) for the product formation in terms of absorbance yields k_2' instead of k_2 in the normal integrated rate equation (S6).

References:

[1] Reeves, R. L.; Harkaway, S. A.; Klingbiel, R. T. Phase transition autocatalysis of the hydrolysis of some esters of azo dyes, *J. Am. Chem. Soc.* **1978**, 100, 3879-3881.