Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for P.J.H Williams et al, "Continuous Addition Kinetic Elucidation: Catalyst and Reactant Order, Rate Constant, and Poisoning from a Single Experiment"

Mathematical Results and Derivations

Derivations of reactant concentration vs time and $t_{1/2}$
Solution for $m = 1$

$$-\frac{\mathrm{d}R(t)}{\mathrm{d}t} = kR(t)C(t)^n \tag{1}$$

$$C(t) = pt \tag{2}$$

Substitute (2) into (1) and separate variables:

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = -kR(t)(pt)^n \tag{3}$$

$$\int_{R_0}^{R(t)} \frac{1}{R}\mathrm{d}R = -kp^n \int_0^t t^n \mathrm{d}t \tag{4}$$

$$[\ln R]_{R_0}^{R(t)} = -kp^n \left[\frac{t^{n+1}}{n+1}\right]_0^t \tag{5}$$

$$\ln\frac{R(t)}{R_0} = -kp^n \frac{t^{n+1}}{n+1} \tag{6}$$

$$\frac{R(t)}{R_0} = \exp\left(-\frac{kp^n t^{n+1}}{n+1}\right) \tag{7}$$

To find $t_{1/2}$:

$$\frac{1}{2} = \exp\left(-\frac{kp^n t_{1/2}^{n+1}}{n+1}\right) \tag{8}$$

$$-\ln 2 = -\frac{kp^n t_{1/2}^{n+1}}{n+1} \tag{9}$$

$$t_{1/2}^{n+1} = \frac{(n+1)\ln 2}{kp^n} \tag{10}$$

$$t_{1/2} = p^{-\frac{n}{n+1}} \left(\frac{(n+1)\ln 2}{k}\right)^{\frac{1}{n+1}} \tag{11}$$

Estimate k from $t_{1/2}$:

$$k = \frac{(n+1)\ln 2}{t_{1/2}^{n+1} p^n} \tag{12}$$

Let $T = t/t_{1/2}$, and substitute $t = t_{1/2}T$ into (7):

$$\frac{R(t)}{R_0} = \exp\left(-\frac{kp^n\left(t_{1/2}T\right)^{n+1}}{(n+1)}\right) \tag{13}$$

$$= \exp\left(-\frac{kp^n\left(\left[p^{-\frac{n}{n+1}}\left(\frac{(n+1)\ln 2}{k}\right)^{\frac{1}{n+1}}\right]T\right)^{n+1}}{(n+1)}\right) \tag{14}$$

$$= \exp\left(-\frac{kp^n p^{-n}\left(\frac{(n+1)\ln 2}{k}\right)T^{n+1}}{(n+1)}\right) \tag{15}$$

$$= \exp\left(-T^{n+1}\ln 2\right) = 2^{-T^{n+1}} \tag{16}$$

$$= \exp\left(-(t/t_{1/2})^{n+1}\ln 2\right) = 2^{-(t/t_{1/2})^{n+1}} \tag{17}$$

Solution for $m \neq 1$

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = -kR(t)^m C(t)^n = -kR(t)^m (pt)^n \tag{18}$$

$$\int_{R_0}^{R(t)} R^{-m}\mathrm{d}R = -kp^n \int_0^t t^n \mathrm{d}t \tag{19}$$

$$\left[\frac{R^{-m+1}}{1-m}\right]_{R_0}^{R(t)} = -kp^n\left[\frac{t^{n+1}}{n+1}\right]_0^t \tag{20}$$

$$\frac{R(t)^{-m+1}}{1-m} - \frac{R_0^{-m+1}}{1-m} = -kp^n\frac{t^{n+1}}{n+1} \tag{21}$$

$$R(t)^{-m+1} - R_0^{-m+1} = (m-1)k\frac{p^n t^{n+1}}{n+1} \tag{22}$$

$$R_0^{-m+1}\left(\left(\frac{R(t)}{R_0}\right)^{-m+1} - 1\right) = (m-1)k\frac{p^n t^{n+1}}{n+1} \tag{23}$$

$$\frac{R(t)}{R_0} = \left(1 + \frac{(m-1)kp^n t^{n+1}}{R_0^{-m+1}(n+1)}\right)^{-\frac{1}{m-1}} \tag{24}$$

$$= \left|1 + \frac{(m-1)kp^n t^{n+1}}{R_0^{-m+1}(n+1)}\right|^{-\frac{1}{m-1}} \tag{25}$$

The last form with the absolute value may avoid difficulties with complex values in fitting routines. In the case of $m \leq 0$, the above formula only holds up to the time t_{end}, after which the concentration is zero.

$$t_{\mathrm{end}} = \left(\frac{R_0^{1-m}(n+1)}{(1-m)kp^n}\right)^{1/(n+1)} \tag{26}$$

Using $\lim_{i\to 0}(1+ai)^{-1/i} = \exp(-a)$, the limit of (24) as $m \to 1$ is seen to be the $m = 1$ formula (7).

Solve for $t_{1/2}$:

$$\frac{1}{2} = \left(\frac{(m-1)kp^n t_{1/2}^{n+1}}{R_0^{-m+1}(n+1)} + 1\right)^{-\frac{1}{m-1}} \tag{27}$$

$$\frac{1}{2^{m-1}} = \left(\frac{(m-1)kp^n t_{1/2}^{n+1}}{R_0^{-m+1}(n+1)} + 1\right)^{-1} \tag{28}$$

$$2^{m-1} = \frac{(m-1)kp^n t_{1/2}^{n+1}}{R_0^{-m+1}(n+1)} + 1 \tag{29}$$

$$t_{1/2} = \left(\frac{\left(2^{m-1}-1\right) R_0^{-m+1}(n+1)}{kp^n(m-1)}\right)^{\frac{1}{n+1}} \tag{30}$$

Estimate k from $t_{1/2}$:

$$k = \frac{\left(2^{m-1}-1\right) R_0^{-m+1}(n+1)}{t_{1/2}^{n+1} p^n (m-1)} \tag{31}$$

Similar to the above, $t = t_{1/2}T$ is substituted into (24):

$$\frac{R(t)}{R_0} = \left(\frac{(m-1)kp^n \left(t_{1/2}T\right)^{n+1}}{R_0^{-m+1}(n+1)} + 1\right)^{-\frac{1}{m-1}} \tag{32}$$

$$= \left(\frac{(m-1)kp^n \left(\left[\left(\frac{\left(2^{m-1}-1\right)R_0^{-m+1}(n+1)}{kp^n(m-1)}\right)^{\frac{1}{n+1}}\right] T\right)^{n+1}}{R_0^{-m+1}(n+1)} + 1\right)^{-\frac{1}{m-1}} \tag{33}$$

$$= \left(\frac{(m-1)kp^n \left(\frac{\left(2^{m-1}-1\right)R_0^{-m+1}(n+1)}{kp^n(m-1)} T^{n+1}\right)}{R_0^{-m+1}(n+1)} + 1\right)^{-\frac{1}{m-1}} \tag{34}$$

$$= \left(1 + \left(2^{m-1}-1\right) T^{n+1}\right)^{-\frac{1}{m-1}} \tag{35}$$

$$= \left(1 + \left(2^{m-1}-1\right) (t/t_{1/2})^{n+1}\right)^{-\frac{1}{m-1}} \tag{36}$$

Again, taking the limit as $m \to 1$ gives the first-order result (16).

Combined equations

As functions of the parameters:

$$R(t) = \begin{cases} R_0 \exp\left(-\frac{p^n k t^{n+1}}{n+1}\right), & m = 1 \\ R_0 \left(1 + \frac{(m-1)kp^n t^{n+1}}{R_0^{-m+1}(n+1)}\right)^{-\frac{1}{m-1}}, & m \neq 1 \end{cases} \tag{37}$$

In terms of $t/t_{1/2}$:

$$\frac{R(t)}{R_0} = \begin{cases} 2^{-\left(t/t_{1/2}\right)^{n+1}}, & m = 1 \\ \left(1 + \left(2^{m-1} - 1\right)\left(t/t_{1/2}\right)^{n+1}\right)^{-\frac{1}{m-1}} & m \neq 1 \end{cases} \tag{38}$$

$t_{1/2}$

$$t_{1/2} = \begin{cases} p^{-\frac{n}{n+1}} \left(\frac{(n+1)\ln 2}{k}\right)^{\frac{1}{n+1}}, & m = 1 \\ \left(\frac{\left(2^{m-1}-1\right)R_0^{-m+1}(n+1)}{kp^n(m-1)}\right)^{\frac{1}{n+1}}, & m \neq 1 \end{cases} \tag{39}$$

k from $t_{1/2}$

$$k = \begin{cases} \frac{(n+1)\ln 2}{t_{1/2}^{n+1} p^n}, & m = 1 \\ \frac{\left(2^{m-1}-1\right)R_0^{-m+1}(n+1)}{t_{1/2}^{n+1} p^n (m-1)}, & m \neq 1 \end{cases} \tag{40}$$

Derivation of relationship between $t_{1/2}$, t_k and t_p

Case of $m = 1$

In a conventional experiment at catalyst concentration C_ref

$$-\frac{\mathrm{d}R(t)}{\mathrm{d}t} = kR_0C_\mathrm{ref}^n = k'R_0 \tag{41}$$

where $k' = kC_\mathrm{ref}^n$ is the pseudo-first-order rate constant. The half-life is well known to be $t_k = \ln(2)/k'$ and we define the characteristic pumping time t_p as the time to add catalyst to concentration C_ref, i.e., $t_\mathrm{p} = C_\mathrm{ref}/p$. Therefore

$$t_\mathrm{k}t_\mathrm{p}^n = \frac{\ln(2)}{kC_\mathrm{ref}^n}\left(\frac{C_\mathrm{ref}}{p}\right)^n \tag{42}$$

$$= \frac{\ln(2)}{kp^n} \tag{43}$$

But the half-life in the CAKE experiment is

$$t_{1/2} = \frac{1}{p}\left(\frac{p\,(n+1)\ln 2}{k}\right)^{\frac{1}{n+1}} \tag{44}$$

$$t_{1/2}^{n+1} = \frac{(n+1)\ln 2}{kp^n} \tag{45}$$

and comparing with the above, we see

$$t_{1/2}^{n+1} = (n+1)t_\mathrm{k}t_\mathrm{p}^n \tag{46}$$

Case of $m \neq 1$

The half life for the general mth order reaction is known to be (Laidler)

$$t_\mathrm{k} = \frac{2^{m-1} - 1}{(m-1)R_0^{m-1}k'} \tag{47}$$

and combining with t_p^n gives

$$t_\mathrm{k} t_\mathrm{p}^n = \frac{2^{m-1}-1}{(m-1)R_0^{m-1} k C_\mathrm{ref}^n} \left(\frac{C_\mathrm{ref}}{p}\right)^n \tag{48}$$

$$= \frac{2^{m-1}-1}{(m-1)R_0^{m-1} k p^n} \tag{49}$$

Compare with

$$t_{1/2} = \left(\frac{\left(2^{m-1}-1\right) R_0^{-m+1}(n+1)}{kp^n(m-1)}\right)^{\frac{1}{n+1}} \tag{50}$$

$$t_{1/2}^{n+1} = \frac{\left(2^{m-1}-1\right)(n+1)}{kp^n R_0^{m-1}(m-1)} \tag{51}$$

and we again find

$$t_{1/2}^{n+1} = (n+1) t_\mathrm{k} t_\mathrm{p}^n \tag{52}$$

To show $t_{1/2} \geq \min(t_\mathrm{k}, t_\mathrm{p})$ and $t_{1/2} \leq 1.4447 \max(t_\mathrm{k}, t_\mathrm{p})$

It is simplest to work with the logs of these quantities:

$$(n+1)\ln t_{1/2} = \ln(n+1) + \ln t_\mathrm{k} + n \ln t_\mathrm{p} \tag{53}$$

$$\ln t_{1/2} = \ln(n+1)^{1/(n+1)} + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln t_\mathrm{p} \tag{54}$$

Consider first the case where $t_\mathrm{k} \geq t_\mathrm{p}$ or $t_\mathrm{k}/t_\mathrm{p} = q$ with $q \geq 1$. We want to show that $t_{1/2} \geq t_\mathrm{p}$

$$\ln t_{1/2} = \ln(n+1)^{1/(n+1)} + \frac{1}{n+1}\ln q t_\mathrm{p} + \frac{n}{n+1}\ln t_\mathrm{p} \tag{55}$$

$$= \ln(n+1)^{1/(n+1)} + \frac{1}{n+1}\ln q + \frac{1}{n+1}\ln t_\mathrm{p} + \frac{n}{n+1}\ln t_\mathrm{p} \tag{56}$$

$$= \ln\left[q(n+1)\right]^{1/(n+1)} + \frac{1}{n+1}\ln t_\mathrm{p} + \frac{n}{n+1}\ln t_\mathrm{p} \tag{57}$$

$$= \ln\left[q(n+1)\right]^{1/(n+1)} + \ln t_\mathrm{p} \tag{58}$$

Now $q \geq 1$, $n \geq 0$ so $q(n+1) \geq 1$. Raising any number ≥ 1 to a positive power gives a number ≥ 1, so $\left[q(n+1)\right]^{1/(n+1)} \geq 1$, $\ln\left[q(n+1)\right]^{1/(n+1)} \geq 0$ and so

$$\ln t_{1/2} \geq \ln t_\mathrm{p} \tag{59}$$

$$t_{1/2} \geq t_\mathrm{p} \tag{60}$$

(using the monotonicity of the ln function).

For this case $t_\mathrm{k} \geq t_\mathrm{p}$ we also want to know what the largest $t_{1/2}$ value can be:

$$\ln t_{1/2} = \ln(n+1)^{1/(n+1)} + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln\frac{t_\mathrm{k}}{q} \tag{61}$$

$$= \ln(n+1)^{1/(n+1)} + \frac{n}{n+1}\ln\frac{1}{q} + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln t_\mathrm{k} \tag{62}$$

$$= \ln\frac{(n+1)^{1/(n+1)}}{q^{n/(n+1)}} + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln t_\mathrm{k} \tag{63}$$

$$= \ln\frac{(n+1)^{1/(n+1)}}{q^{n/(n+1)}} + \ln t_\mathrm{k} \tag{64}$$

For fixed n, $(n+1)^{1/(n+1)}/q^{n/(n+1)}$ decreases as q increases from 1 (its derivative is explicitly negative) and so its largest value occurs for $q = 1$, when it equals $(n+1)^{1/(n+1)}$. The value of $(n+1)^{1/(n+1)}$ is always larger than or equal to one, and has its maximum when

$$0 = \frac{\mathrm{d}(n+1)^{1/(n+1)}}{\mathrm{d}n} = (n+1)^{1/(n+1)}\frac{(1-\ln(n+1))}{(n+1)^2} \tag{65}$$

$$0 = 1 - \ln(n+1) \tag{66}$$

$$n + 1 = \exp(1) \tag{67}$$

$$n = \exp(1) - 1 = 1.718 \tag{68}$$

The maximum value is therefore

$$(n+1)^{1/(n+1)} = \exp(1)^{1/\exp(1)} = 1.4447 \tag{69}$$

and therefore the largest value of $t_{1/2}$ is $1.445 t_\mathrm{k}$, which occurs when $t_\mathrm{k} = t_\mathrm{p}$ and $n = 1.718$.

For the case where $t_\mathrm{p} \geq t_\mathrm{k}$ or $t_\mathrm{p}/t_\mathrm{k} = q$ with $q \geq 1$. We want to show that $t_{1/2} \geq t_\mathrm{k}$. We proceed similarly to the above.

$$\ln t_{1/2} = \ln(n+1)^{1/(n+1)} + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln q t_\mathrm{k} \tag{70}$$

$$= \ln(n+1)^{1/(n+1)} + \frac{n}{n+1}\ln q + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln t_\mathrm{k} \tag{71}$$

$$= \ln\left[q^{n/(n+1)}(n+1)^{1/(n+1)}\right] + \frac{1}{n+1}\ln t_\mathrm{k} + \frac{n}{n+1}\ln t_\mathrm{k} \tag{72}$$

$$= \ln\left[q^{n/(n+1)}(n+1)^{1/(n+1)}\right] + \ln t_\mathrm{k} \tag{73}$$

Now $q \geq 1$, $n \geq 0$ so $q^{n/(n+1)} \geq 1$, $(n+1)^{1/(n+1)} \geq 1$ and therefore $q^{n/(n+1)}(n+1)^{1/(n+1)} \geq 1$ leading to

$$\ln t_{1/2} \geq \ln t_\mathrm{k} \tag{74}$$

$$t_{1/2} \geq t_\mathrm{k} \tag{75}$$

For this case $t_\mathrm{p} \geq t_\mathrm{k}$ we also want to know what the largest $t_{1/2}$ value can be:

$$\ln t_{1/2} = \ln(n+1)^{1/(n+1)} + \frac{1}{n+1} \ln \frac{t_\mathrm{p}}{q} + \frac{n}{n+1} \ln t_\mathrm{p} \tag{76}$$

$$= \ln(n+1)^{1/(n+1)} + \frac{1}{n+1} \ln \frac{1}{q} + \frac{1}{n+1} \ln t_\mathrm{p} + \frac{n}{n+1} \ln t_\mathrm{p} \tag{77}$$

$$= \ln \left[(n+1)/q\right]^{1/(n+1)} + \frac{1}{n+1} \ln t_\mathrm{p} + \frac{n}{n+1} \ln t_\mathrm{p} \tag{78}$$

$$= \ln \left[(n+1)/q\right]^{1/(n+1)} + \ln t_\mathrm{p} \tag{79}$$

For fixed n, $[(n+1)/q]^{1/(n+1)}$ decreases as q increases from 1 (its derivative is explicitly negative) and so its largest value occurs for $q = 1$, when it equals $(n+1)^{1/(n+1)}$, which as above has a maximum value of 1.4447. Therefore in this case, the largest value of $t_{1/2}$ is $1.4447 t_\mathrm{p}$.