Supporting Information

The Effects of Ligand Decomposition on the Pseudo-First Order Profile of a Ligand Substitution Reaction: A "silent killer" in the background

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Derivation of Equation (4)

For the system

$$A + L \xrightarrow{k_1} \text{products}$$

$$L \xrightarrow{k_L} \text{decomposition products}$$

$$\frac{d[A]}{dt} = -k_1[A][L]$$

$$\frac{d[L]}{dt} = -k_1[A][L] - k_L[L]$$

$$\frac{d[L]}{d[A]} = \frac{-k_1[A][L] - k_L[L]}{-k_1[A][L]}$$

$$\frac{d[L]}{d[A]} = 1 + \frac{k_L}{k_1[A]}$$

$$d[L] = \left(1 + \frac{k_L}{k_1[A]}\right) d[A]$$

Integrating gives $[L] = [A] + \frac{k_L}{k_1}\ln[A] + c_1$ where c_1 is a constant.

Now,

$$\frac{d[A]}{dt} = -k_1[A][L]$$

$$= -k_1[A]\left([A] + \frac{k_L}{k_1}\ln[A] + c_1\right)$$

Then,

$$\frac{d[A]}{dt} = -k_1[A]^2 - k_L[A]\ln[A] - k_1[A]c_1$$

$\int \frac{d[A]}{k_1\,[A]^2 + k_L[A]\ln[A] + k_1[A]c_1} = -t + c_2$ where c_2 is a constant.

This integral cannot be determined analytically (solved by quadrature).

Figure S1.

Best fit of the simulated data at $k_1[L]_0/k_L = 1$ assuming that the reaction fits a simple first-order equation, giving $k_{1st} = 8.363 \times 10^{-3}$ min^{-1}. The simulated data has been fitted for the first 5 half lives of the reaction. The following parameters were fixed to obtain the simulated data: $[L]_o = 5.00 \times 10^{-4}$ M, $[A]_0 = 5.00 \times 10^{-5}$ M, dt = 1×10^{-3} min, $k_1 = 12.4$ M^{-1} min^{-1} and $k_L = 6.20 \times 10^{-3}$ min^{-1}. Selected data points are shown for clarity.

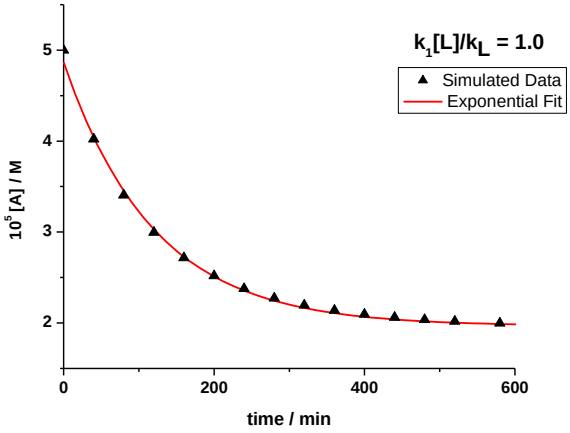

Figure S2

Best fit of the simulated data at $k_1[L]_0/k_L = 0.5$ assuming that the reaction fits a simple first-order equation, giving $k_{1st} = 1.446 \times 10^{-2}$ min^{-1}. The simulated data has been fitted for the first five half lives of the reaction. The following parameters were fixed to obtain the simulated data: $[L]_o = 5.00 \times 10^{-4}$ M, $[A]_0 = 5.00 \times 10^{-5}$ M, dt = 1×10^{-3} min, $k_1 = 12.4$ M^{-1} min^{-1} and $k_L = 0.0124$ min^{-1}. Selected data points are shown for clarity.

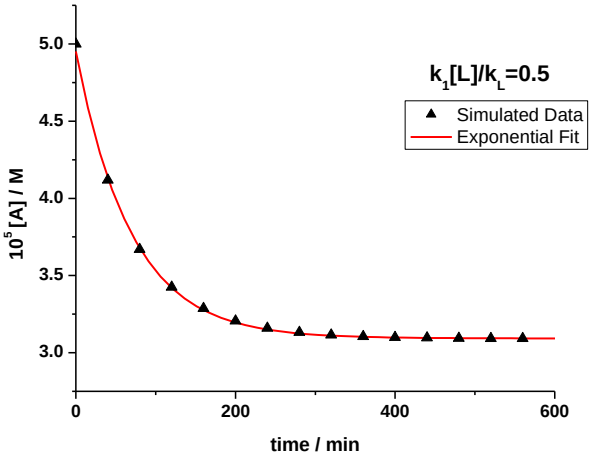

Figure S3

Best fit of the simulated data at $k_1[L]_0/k_L = 5.0$ assuming that the reaction fits a simple first-order equation, giving $k_{1st} = 5.187 \times 10^{-3}$ min^{-1}. The simulated data has been fitted for the first five half lives of the reaction. The following parameters were fixed to obtain the simulated data: $[L]_o = 5.00 \times 10^{-4}$ M, $[A]_0 = 5.00 \times 10^{-5}$ M, dt = 1×10^{-3} min, $k_1 = 12.4$ M^{-1} min^{-1} and $k_L = 1.24 \times 10^{-3}$ min^{-1}. Selected data points are shown for clarity.

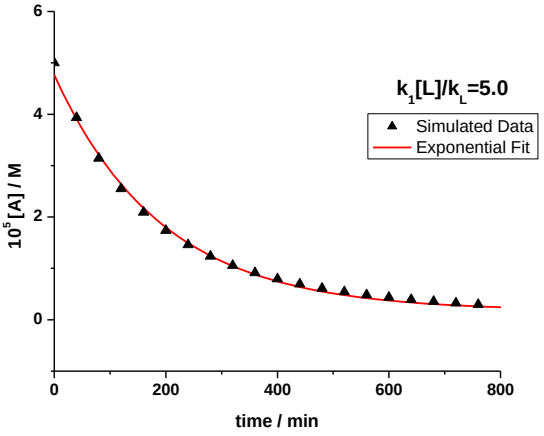

Figure S4

An expanded view of Figure 5c) in the main text.