What is the order of a reaction?

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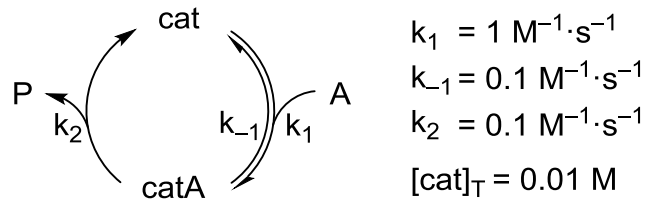
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Mathematical deductions of elasticity coefficients

1. **Figure 1**

$k_1 = 1\ M^{-1}{\cdot}s^{-1}$

$k_{-1} = 0.1\ M^{-1}{\cdot}s^{-1}$

$k_2 = 0.1\ M^{-1}{\cdot}s^{-1}$

$[cat]_T = 0.01\ M$

For the popular unireactant catalytic reaction following the Briggs-Haldane kinetics, the rate law is given by equation 3, obtained by using the Bodenstein steady-state approximation and the mass balance for the catalytic species:

Steady-state approximation: $\dfrac{d[cat]}{dt} = (k_{-1} + k_2)[catA] - k_1[A][cat] \approx 0$ (1)

Mass Balance of catalytic species: $[cat]_T = [cat] + [catA]$ (2)

Rate law: $r = \dfrac{d[P]}{dt} = \dfrac{k_1 k_2 [A][cat]_T}{k_{-1} + k_2 + k_1[A]} = \dfrac{V_{max}[A]}{K_M + [A]}$ (3)

where $K_M = \dfrac{k_{-1} + k_2}{k_1}$ and $V_{max} = k_2[cat]_T$

Order of the reaction in [A]:

$\varepsilon^r_{[A]} = \dfrac{dr}{d[A]} \cdot \dfrac{[A]}{r} = \dfrac{V_{max}K_M}{(K_M + [A])^2} \cdot \dfrac{[A](K_M + [A])}{V_{max}[A]} = \dfrac{K_M}{K_M + [A]}$ (4)

2. Figure 2

$K_D = 10\ M$

$k_1\ = 1\ M^{-1}\cdot s^{-1}$

$k_{-1} = 0.1\ s^{-1}$

$k_2\ = 0.1\ s^{-1}$

$[A]_o = 1\ M$
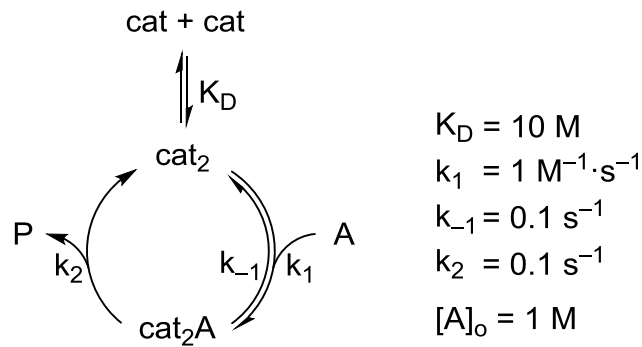
The Bodenstein steady-state approximation is applied to the catalytic cycle (equation 1) and the quasi-equilibrium assumption to the out-cycle equilibrium (equation 2). The rate law for the reaction (equation 4) is derived using these two equations and the mass balance (equation 3) for the catalytic species.

Steady-state approximation: $\dfrac{d[cat_2]}{dt} = (k_{-1} + k_2)[cat_2A] - k_1[A][cat_2] \approx 0$ (1)

Quasi-equilibrium assumption: $K_D = \dfrac{[cat_2]}{[cat]^2}$ (2)

Mass Balance of catalytic species: $[cat]_T = [cat] + 2[cat_2] + 2[cat_2A]$ (3)

Rate law: $r = \dfrac{d[P]}{dt} = \dfrac{4k_1k_2K_D[A][cat]_T^2}{(k_{-1}+k_2)\left(1+\sqrt{1+4a[cat]_T}\right)^2}$; where $a = 2K_D\left(1+ \dfrac{k_1[A]}{k_{-1}+k_2}\right)$ (4)

Order of the reaction in $[cat]_T$: $\varepsilon^r_{[cat]_T} = \dfrac{dr}{d[cat]_T} \cdot \dfrac{[cat]_T}{r} = 1 + \dfrac{1}{\sqrt{1+4a[cat]_T}}$ (5)

3. Figure 3

$k_1 = 0.01 \ M^{-1}{\cdot}s^{-1}$

$k_{-1} = 0.2 \ M^{-1}{\cdot}s^{-1}$

$k_2 = 1 \ M^{-1}{\cdot}s^{-1}$

$[A]_o = 1 \ M$
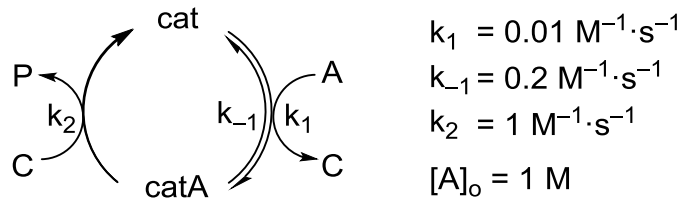
The rate law for a reaction where one of the byproducts of one of the steps of the cycle is used as a reactant in a subsequent catalytic step (equation 3) is obtained by combining the Bodenstein steady-state approximation (equation 1) with the mass balance for the catalytic species (equation 2) and assuming [C]=[catA].
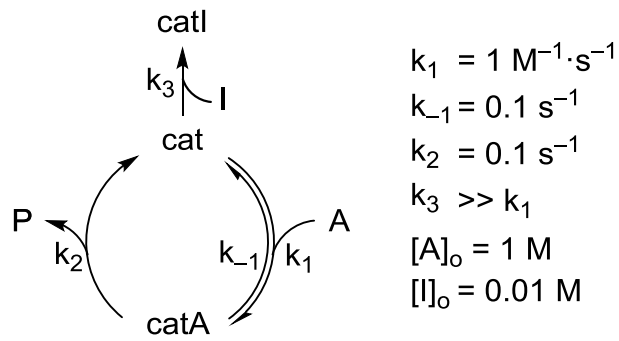
Steady-state approximation: $\dfrac{d[cat]}{dt} = (k_{-1} + k_2)[catA][C] - k_1[A][cat] \approx 0$ （1)

Mass Balance of catalytic species: $[cat]_T = [cat] + [catA]$ （2)

Rate law: $r = \dfrac{d[P]}{dt} = \dfrac{4k_2[cat]_T^2}{\left(1+\sqrt{1+4a[cat]_T}\right)^2}$; where $a = \dfrac{k_{-1}+k_2}{k_1[A]}$ （3)

Order of the reaction in [cat]$_T$: $\varepsilon_{[cat]_T}^r = \dfrac{dr}{d[cat]_T} \cdot \dfrac{[cat]_T}{r} = 1 + \dfrac{1}{\sqrt{1+4a[cat]_T}}$ （4)

4. Figure 4

$k_1 = 1\ M^{-1}\cdot s^{-1}$

$k_{-1} = 0.1\ s^{-1}$

$k_2 = 0.1\ s^{-1}$

$k_3 \gg k_1$

$[A]_o = 1\ M$

$[I]_o = 0.01\ M$

When there is an impurity that irreversibly deactivates the catalyst, the equation for the rate law (equation 2) is similar to the one for the catalytic cycle in Figure 1. However, in this case the total amount of catalyst available is the amount of added catalyst minus the amount deactivated by the inhibitor in a 1:1 ratio (equation 1).

$$[cat]_T = [cat]_{added} - [I]_o \tag{1}$$

Rate law: $r = \dfrac{d[P]}{dt} = \dfrac{V_{max}[A]}{K_M+[A]} = \dfrac{k_2[cat]_T[A]}{K_M+[A]} = \dfrac{k_2[A]([cat]_{added}-[I]_o)}{K_M+[A]} \tag{2}$

where $K_M = \dfrac{k_{-1}+k_2}{k_1}$

Order of the reaction in [cat]$_{added}$:

$$\varepsilon^r_{[cat]_{added}} = \dfrac{dr}{d[cat]_{added}} \cdot \dfrac{[cat]_{added}}{r} = \dfrac{[cat]_{added}}{([cat]_{added}-[I]_o)} \tag{3}$$