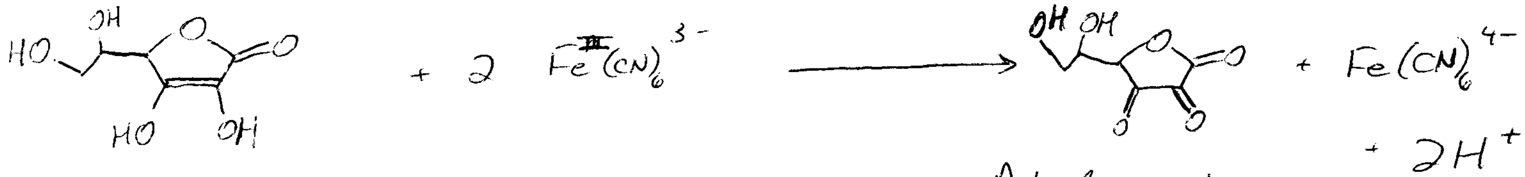
Notes on Kinetics: Derivation of Relevant Equations

The reaction:



Ascorbic acid
Vitamin C
"H_2Asc"

Dehydroascorbic acid: "Asc"

- Ascorbic acid is a reducing agent because of the electron-donating $-\ddot{\underset{..}{O}}H$ groups on the C=C double bond.
- Ferricyanide is a 17-electron complex. Its highest occupied molecular orbital is half-full and low in energy: easily accepts one electron.

Empirically (at constant pH):

$$-\frac{d[H_2Asc]}{dt} = -\frac{1}{2}\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}[H_2Asc][Fe(CN)_6^{3-}]$$

(rate of disappearance)

Second-order rate law

Note: $-\frac{d[H_2Asc]}{dt} = -\frac{1}{2}\frac{[Fe(CN)_6^{3-}]}{dt}$ can be deduced from the reaction stoichiometry.

$= k_{obs}[H_2Asc][Fe(CN)_6^{3-}]$ cannot be deduced a priori; depends on reaction mechanism.

The mechanistic hypothesis involves three steps. (The third is arguably two steps, but treating them together won't affect the overall picture. Think about why.)

1) $H_2Asc \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HAsc^- + H^+$ Very fast, reversible

2) $HAsc^- + Fe(CN)_6^{3-} \xrightarrow{k_2} HAsc^{\bullet} + Fe(CN)_6^{4-}$

Irreversible;
slow-rate-limiting step

3) $HAsc^{\bullet} + Fe(CN)_6^{3-} \xrightarrow{k_3} Asc + Fe(CN)_6^{4-} + H^+$

Fast; irreversible

How can we derive an expression for $[Fe(CN)_6^{3-}]$ concentration over time?

— Two reactions consume $Fe(CN)_6^{3-}$, so:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_2[HAsc^-][Fe(CN)_6^{3-}] + k_3[HAsc^{\bullet}][Fe(CN)_6^{3-}]$$

We don't have a convenient way to measure $[HAsc^-]$ or $[HAsc^{\bullet}]$. However, for fleeting intermediates at low concentration, we can invoke the steady-state approximation. If a species reacts too rapidly to accumulate in substantial concentration, the rate of its formation is equal to the rate of its removal.

Thus: $\frac{d[HAsc^-]}{dt} = 0$; $\frac{d[HAsc^{\bullet}]}{dt} = 0$

Let's get rid of [HAsc˙] first:

$$\text{Rate of formation} = \text{Rate of removal}$$

$$k_2[HAsc^-][Fe(CN)_6^{3-}] = k_3[HAsc^{\cdot}][Fe(CN)_6^{3-}]$$

Recall: $$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_2[HAsc^-][Fe(CN)_6^{3-}] + k_3[HAsc^{\cdot}][Fe(CN)_6^{3-}]$$

Substituting:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = 2k_2[HAsc^-][Fe(CN)_6^{3-}]$$

A similar treatment can be used for $[HAsc^-]$. Recall reactions 1) and 2) above.

$$\text{Rate of formation} = \text{Rate of removal}$$

$$k_1[H_2Asc] = k_{-1}[HAsc^-][H^+] + k_2[HAsc^-][Fe(CN)_6^{3-}]$$

$$= \left(k_{-1}[H^+] + k_2[Fe(CN)_6^{3-}]\right)[HAsc^-]$$

So: $$\frac{k_1[H_2Asc]}{k_{-1}[H^+] + k_2[Fe(CN)_6^{3-}]} = [HAsc^-]$$

Substituting for $[HAsc^-]$ in the rate law:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_1k_2}{k_{-1}[H^+] + k_2[Fe(CN)_6^{3-}]}[H_2Asc][Fe(CN)_6^{3-}]$$

Can we simplify this expression?

$$-\frac{d[\mathrm{Fe(CN)_6^{3-}}]}{dt} = \frac{2\,k_1 k_2}{k_{-1}[\mathrm{H^+}] + \cancel{k_2[\mathrm{Fe(CN)_6^{3-}}]}}\,[\mathrm{H_2Asc}][\mathrm{Fe(CN)_6^{3-}}]$$

$[\mathrm{H^+}] > [\mathrm{Fe(CN)_6^{3-}}]$ under the reaction conditions

$k_{-1} >> k_2$ k_{-1} is the rate constant for a proton transfer, and these are *very* fast; k_2 is the constant for the rate-limiting step.

$$-\frac{d[\mathrm{Fe(CN)_6^{3-}}]}{dt} = \frac{2\,k_1 k_2}{k_{-1}[\mathrm{H^+}]}\,[\mathrm{H_2Asc}][\mathrm{Fe(CN)_6^{3-}}]$$

Recall that at equilibrium,

$$k_1[\mathrm{H_2Asc}] = k_{-1}[\mathrm{H^+}][\mathrm{HAsc^-}];$$

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{HAsc^-}][\mathrm{H^+}]}{[\mathrm{H_2Asc}]} = K_a = 6.76 \times 10^{-5}\ \mathrm{M}\ @\ 25^\circ\mathrm{C}$$

$$-\frac{d[\mathrm{Fe(CN)_6^{3-}}]}{dt} = \frac{2\,K_a}{[\mathrm{H^+}]} \cdot k_2 \cdot [\mathrm{Fe(CN)_6^{3-}}][\mathrm{H_2Asc}]$$

Units: $\mathrm{moles \cdot L^{-1} \cdot s^{-1}}$ $\quad \dfrac{\mathrm{moles \cdot L^{-1}}}{\mathrm{moles \cdot L^{-1}}} \cdot k_2 \cdot (\mathrm{moles \cdot L^{-1}})(\mathrm{moles \cdot L^{-1}})$

k_2 is in $\mathrm{L \cdot mole^{-1} \cdot s^{-1}}$

So, based on a mechanistic hypothesis, we've just derived an equation with the form of a second-order rate law:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}[Fe(CN)_6^{3-}][H_2Asc],$$

$$\text{where } k_{obs} = \frac{2K_a k_2}{[H^+]}$$

Since we set $[H^+]$ by adding a strong acid (so that $[H^+]$ doesn't change much over the course of the reaction), and since we can look up K_a for ascorbic acid, we can calculate k_2, the rate constant for electron transfer, from the observed rate constant (k_{obs}).

Back to the integrated rate law, expressing $[Fe(CN)_6^{3-}]$ versus t:

- Second-order reaction: $H_2Asc + 2\,Fe(CN)_6^{3-} \longrightarrow$ products

Let $A_t = [H_2Asc]_t$; $B_t = [Fe(CN)_6^{3-}]_t$, for simplicity.

$$-\frac{1}{2}\frac{dB_t}{dt} = \frac{-dA_t}{dt} = k_{obs} A_t B_t$$

$$-\frac{dB_t}{2A_t B_t} = k_{obs}\,dt$$

Can we put A_t in terms of B_t ?

$$A_t = A_o - \underset{\substack{\uparrow \\ \text{Amount consumed at time} = t}}{(A_o - A_t)} \qquad (\text{Trivially}: A_t = A_t)$$

$$(A_o - A_t) = \frac{1}{2}(B_o - B_t)$$

$$A_t = A_o - \frac{1}{2}(B_o - B_t)$$

So: $$k_{obs}\,dt = \frac{-dB_t}{2(A_o - \frac{1}{2}B_o + \frac{1}{2}B_t)B_t} = \frac{-dB_t}{(2A_o - B_o + B_t)B_t}$$

Solution: $$k_{obs}t = \frac{1}{2A_o - B_o}\ln\frac{A_t B_o}{A_o B_t}$$

(see also: Steinfeld, J.I. et al. "Chemical Kinetics and Dynamics," 2nd ed. (Prentice-Hall, Upper Saddle River, NJ, 1999), Ch. 1).

- Remember, we're observing B_t.

  Can we relate A_0 to B_0?

  - Each molecule of H_2Asc reacts with two $[Fe(CN)_6^{3-}]$.
  - If the concentration of $[Fe(CN)_6^{3-}]$ is more than twice that of H_2Asc at $t=0$, then some $[Fe(CN)_6^{3-}]$ will be left after the reaction is over. We'll denote this as B_∞.

$$B_0 - 2A_0 = B_\infty$$

$$k_{obs}t = \frac{1}{2A_0 - B_0} \ln \frac{A_t B_0}{A_0 B_t} = \frac{1}{-B_\infty} \ln \frac{A_t B_0}{A_0 B_t}$$

$$\ln \frac{A_t B_0}{A_0 B_t} = -B_\infty k_{obs} t$$

$$\frac{A_t B_0}{A_0 B_t} = \exp(-B_\infty k_{obs} t)$$

Rearranging terms:

$$B_t = \frac{A_t B_0}{A_0 \exp(-B_\infty k_{obs} t)}$$

Recall: $A_t = A_0 - \frac{1}{2}B_0 + \frac{1}{2}B_t$

$$= \frac{1}{2}\left(2A_0 - B_0 + B_t\right) \quad ; \quad 2A_0 - B_0 = -B_\infty$$

Thus: $$B_t = \frac{\frac{1}{2}\left(-B_\infty + B_t\right)\left(B_0\right)}{A_0 \exp\left(-B_\infty k_{obs} t\right)}$$

Multiply top and bottom by $\frac{2}{B_0}$

$$B_t = \frac{-B_\infty + B_t}{\frac{2A_0}{B_0} \exp\left(-B_\infty k_{obs} t\right)}$$

$B_0 - 2A_0 = B_\infty$;

$2A_0 = B_0 - B_\infty$

$$B_t = \frac{-B_\infty + B_t}{\frac{B_0 - B_\infty}{B_0} \exp\left(-B_\infty k_{obs} t\right)}$$

$$B_t\left\{ \frac{B_0 - B_\infty}{B_0} \exp\left(-B_\infty k_{obs} t\right)\right\} = -B_\infty + B_t$$

$$B_t - B_t \left\{ \quad \right\} = B_\infty$$

$$B_t \left(1 - \left\{ \ \right\}\right) = B_\infty$$

$$B_t = \frac{B_\infty}{1 - \left\{ \frac{B_0 - B_\infty}{B_0} \exp\left(-B_\infty k_{obs} t\right) \right\}}$$

Remember, B_t is what we're observing spectrophotometrically.
Absorbance is proportional to $[Fe(CN)_6^{3-}]$.
(at 418 nm)

So $[Fe(CN)_6^{3-}]_t$ has been given as an equation with
- one variable (under controlled conditions)
- several constants

We don't want to wait for $t = \infty$, so the absorbance at ∞ and k_{obs} are derived from the curve-fitting.