Practical Kinetics and Mechanisms of Chemical and Enzymatic Reactions

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To my parents,
Nina and Dmitry

CONTENTS

SOLUTIONS OF SELECTED PROBLEMS

1-2. $k_{\mathrm{AB+C}} = \frac{\bar{k}T}{h}e^{-\frac{\Delta G^{\neq}_{\mathrm{AB+C}}}{RT}}$. Hence

$$\Delta G^{\neq}_{\mathrm{AB+C}} = RT\left(ln\frac{\bar{k}T}{h} - lnk_{\mathrm{AB+C}}\right);$$

$$\Delta G^{\neq}_{\mathrm{A+BC}} = \Delta G^{\neq}_{\mathrm{AB+C}} + \Delta G^{0} = \Delta G^{\neq}_{\mathrm{AB+C}} - RT\ln K.$$

1-3. If $k_{\mathrm{obs}} = kK$, $k = k_{\mathrm{obs}}/K = 10^{6}/10^{20} = 10^{26}$ M^{-1} s^{-1}. This is far above diffusion limit.

1-4. Arrhenius: $\ln k = \ln A - E_{\mathrm{A}}/RT$; $\frac{\partial lnk}{\partial T} = \frac{E_{\mathrm{A}}}{RT^{2}}$.

Eyring: $lnk = lnT + ln\frac{\bar{k}}{h} - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$; $\frac{\partial lnk}{\partial T} = \frac{1}{T} + \frac{\Delta H^{\neq}}{RT^{2}}$.

Therefore

$$\frac{\partial lnk}{\partial T} = \frac{E_{\mathrm{A}}}{RT^{2}} = \frac{1}{T} + \frac{\Delta H^{\neq}}{RT^{2}}$$

Finally

$$E_{\mathrm{A}} = \Delta H^{\neq} + RT$$

1-5. $k_1 = Ae^{-\frac{E_{\mathrm{A}}}{RT}}$; $k_2 = Ae^{-\frac{(E_{\mathrm{A}}+5.85)}{RT}}$; $\frac{k_1}{k_2}e^{-\frac{5.85(\mathrm{kJ\ mol}^{-1})}{RT}} \sim 10$.

1-7. The sphere volume is $\frac{4}{3}\pi r^{3}$. The density $\rho = M/V = \frac{3\mathrm{M}}{4\pi r^{3}}$. Hence, $r = \sqrt[3]{\frac{3\mathrm{M}}{4\pi\rho}}$. $D = \frac{\bar{k}T}{6\pi\eta r}$. Therefore $D \sim M^{-1/3}$.

1-8. One in both decaborane and alcohol. Two overall.

2-1. $\mathrm{A}_{\mathrm{o}} = \varepsilon_{\mathrm{A}}a_0$; $\mathrm{A}_{\infty} = \varepsilon_{\mathrm{B}}a_0$; $\mathrm{A}_{\mathrm{t}} = \varepsilon_{\mathrm{A}}a_0e^{-kt} + \varepsilon_{\mathrm{B}}a_0(1 - e^{-kt}) = a_0\Delta\varepsilon e^{-kt} + \varepsilon_{\mathrm{B}}a_0$ with $\Delta\varepsilon = \varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}}$. Therefore

$$\ln\{(A_o - A_\infty)/(A_t - A_\infty)\} = ln\frac{\varepsilon_A a_0 - \varepsilon_B a_0}{a_0 \Delta\varepsilon e^{-kt}} = \ln e^{kt} = kt$$

2-2. $k = 0.3$ min^{-1}.

2-3. At $t = t$, [A] = $(a_o - x)$ and [B] = $b_o + x$. Correspondingly

$$-\frac{d(a_0 - x)}{dt} = k_1(a_0 - x) - k_{-1}(b_0 + x) = k_1 a_0 - k_{-1} b_0 - x(k_1 + k_{-1}) = \alpha - x\beta$$

with $\alpha = k_1 a_0 - k_{-1} b_0$ and $\beta = k_1 + k_{-1}$. Therefore

$$-\frac{1}{\beta} \times \frac{d(\alpha - \beta x)}{(\alpha - \beta x)} = dt; \qquad \ln(\alpha - \beta x) = c + \beta t$$

At $t = 0$ $x = 0$, α = c and hence

$$\alpha - \beta x = \alpha e^{-\beta t} \text{ and } x = \frac{\alpha}{\beta}(1 - e^{-\beta t})$$

Substitution gives

$$x = \frac{a_0 k_1 - b_0 k_{-1}}{k_1 + k_{-1}}\left(1 - e^{-(k_1 + k_{-1})t}\right)$$

At $t \to \infty$

$$x_{\text{eq}} = (k_1 a_o - k_{-1} b_o)/(k_1 + k_{-1}).$$

Finally

$$x = x_{\text{eq}}\left(1 - e^{-(k_1 + k_{-1})t}\right).$$

2-5. If Mechanism 1. holds, the amount of B formed should depend on the concentration of X_t (see eq 2.2.3) and the equilibrium constant $K = k_1/k_{-1}$ could be calculated. This should correspond to the ratio of k_1 and k_{-1} found in the kinetic experiment. If Mechanism 2. holds, the amount of B formed is always constant and equal A_t.

2-6. Apply the condition $k_1 = k_2 = k$ to eq 2.4.4. Then

$$d(z \times e^{kt}) = k a_o dt$$

Integration and application of the boundary condition $z = 0$ at $t = 0$ results in

$z = a_0kte^{-kt}$ and $y = x - z = a_0(1 - e^{-kt} - kte^{-kt})$

Differentiation gives the expression for the steady-state time.

2-7. The differential equation for the consumption of A:

$$-d(a_0-x)/dt = k_1(a_0-x) + k_2(a_0-x)^2$$

If $y = (a_0 - x)$, after rearrangement

$$-\frac{dy}{y(k_1 + yk_2)} = dt$$

and

$$\frac{1}{y(k_1 + yk_2)} = \frac{m}{y} + \frac{n}{k_1 + yk_2}$$

Coefficients m and n are found as for the second-order reaction: $m = 1/k_1$ and $-n = k_2/k_1$. Thus, the function easy to integrate is

$$-\frac{1}{k_1}\frac{dy}{y} + \frac{k_2}{k_1} \times \frac{dy}{k_1 + yk_2} = dt$$

And

$$-\frac{1}{k_1}\frac{dy}{y} + \frac{1}{k_1} \times \frac{d(k_1 + yk_2)}{k_1 + yk_2} = dt$$

followed

$$-\frac{1}{k_1}(lny + ln(k_1 + yk_2)) = t + c$$

Using the boundary conditions $y = a_0$ at $t = 0$ one gets

$$ln\frac{a_0[k_1+(a_0-x)k_2]}{(a_0-x)(k_1+a_0k_2)} = k_1t\,; \qquad a_0 - x = \frac{a_0k_1e^{-k_1t}}{k_1+a_0k_2e^{-k_1t}}$$

2-10. At any time $\frac{b}{c} = \frac{k_1}{k_2}$ and $x = b + c$. Combining these two equations one obtains

$$x = \frac{k_1 + k_2}{k_1} b$$

Substitution of the expression for x into $x = a_0(1 - e^{-(k_1+k_2)t})$ affords

$$b = a_0 \frac{k_1}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

2-11. It should be confirmed that the relations

$$-\frac{d(a_0 - x)}{dt} = k_1 a_0 e^{-k_1 t} = \frac{dz}{dt} = \frac{k_1 k_2 a_0}{k_1 - k_2}(e^{-k_2 t} - e^{-k_1 t})$$

hold at the steady state. It follows

$$k_1 a_0 e^{-k_1 t} = \frac{k_1 k_2 a_0}{k_1 - k_2}(e^{-k_2 t} - e^{-k_1 t})$$

and
$$e^{-k_1 t} = \frac{k_2}{k_1 - k_2}(e^{-k_2 t} - e^{-k_1 t})$$

Rearrangement affords

$$k_1 e^{-k_1 t} - k_2 e^{-k_1 t} = k_2 e^{-k_2 t} - k_2 e^{-k_1 t}$$

Finally

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

2-12.
$$x = \frac{a_0(1-e^{(a_0-b_0)kt})}{1-\frac{a_0}{b_0}e^{(a_0-b_0)kt}}$$

1) $a_0 > b_0$
$$x = \frac{-a_0 e^{(a_0-b_0)kt}}{-\frac{a_0}{b_0}e^{(a_0-b_0)kt}} = b_0$$

2) $a_0 < b_0$ $x = a_0$.

3-1. Mass balance A_t = [A]+[AL]; SSA:

$$0 \sim d[\mathrm{AL}]/dt = k_1[\mathrm{A}][\mathrm{L}] - [\mathrm{AL}](k_{-1}+k_2)$$

Two equations, two unknowns. Find expressions for [A] and [AL] at the steady-state

$$d[\mathrm{P}]/dt = k_2[\mathrm{AL}] + k_3[\mathrm{A}]$$

Working with the mass balance equations, one obtains

$$\mathrm{A_t} = [\mathrm{A}]\left(1 + \frac{k_1\mathrm{L}}{k_{-1} + k_2}\right)$$

And

$$[\mathrm{A}] = \frac{k_{-1} + k_2}{k_1\mathrm{L} + k_{-1} + k_2}\mathrm{A_t}; \qquad [\mathrm{AL}] = \frac{k_1\mathrm{L}}{k_1\mathrm{L} + k_{-1} + k_2}\mathrm{A_t}$$

Finally

$$k_{\mathrm{obs}} = \frac{k_3(k_{-1} + k_2) + k_1k_2\mathrm{L}}{k_1\mathrm{L} + k_{-1} + k_2} = \frac{k_3 + \dfrac{k_1k_2}{k_{-1} + k_2}\mathrm{L}}{1 + \dfrac{k_1\mathrm{L}}{k_{-1} + k_2}}$$

3-2. Mass balance $\mathrm{Fe_t} = [\mathrm{Fe^{III}}]+[\mathrm{Oxidized}]$; SSA with respect to Oxidized TAML:

$$0 \sim d[\mathrm{Oxidized}]/dt = k_1[\mathrm{Fe^{III}}][\mathrm{H_2O_2}] - [\mathrm{Oxidized}](k_{-1}+k_2[\mathrm{S}])$$

Since

$$d[\mathrm{P}]/dt = k_2[\mathrm{Oxidized}][\mathrm{S}]$$

one obtains

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{H_2O_2}][\mathrm{S}]}{k_{-1} + k_1[\mathrm{H_2O_2}] + k_2[\mathrm{S}]}\mathrm{Fe_t}$$

Plotting inverse rate versus $[\mathrm{HOOH}]^{-1}$ or $[\mathrm{S}]^{-1}$ allows to calculate k_1 and k_2 from the slope and intercept if $k_{-1} \sim 0$.

3-3. Mass balance $\mathrm{E_t} = [\mathrm{E}]+[\mathrm{ES}]$; $K_\mathrm{s} = [\mathrm{E}][\mathrm{S_t}]/[\mathrm{ES}]$. Therefore $[\mathrm{ES}] = \mathrm{E_tS_t}/(K_\mathrm{s}+\mathrm{S_t})$ and $v = k_2\mathrm{E_tS_t}/(K_\mathrm{s}+\mathrm{S_t})$.

$$K_{\mathrm{m}} = \frac{k_{-1}}{k_1} + \frac{k_2}{k_1};\ K_{\mathrm{S}} = \frac{k_{-1}}{k_1}.\ \text{Hence } K_{\mathrm{m}} = K_{\mathrm{S}} + \frac{k_2}{k_1}.$$

3-4. Mass balance $E_t = [E] + [ES] + [EA]$; SSA:

$$0 \sim d[\mathrm{ES}]/dt = k_1[\mathrm{E}][\mathrm{S}] - [\mathrm{ES}](k_{-1}+k_2)$$

$$0 \sim d[\mathrm{EA}]/dt = k_2[\mathrm{ES}] - k_3[\mathrm{EA}]$$

Three equations, three unknowns. Find expression for [EA] because

$$d[\mathrm{P}]/dt = k_3[\mathrm{EA}]$$

Working with the mass balance equations, one obtains

$$\begin{aligned}\mathrm{E_t} = [\mathrm{E}] + [\mathrm{ES}] + [\mathrm{EA}] = [\mathrm{EA}]\frac{k_3}{k_2}\left(1 + \frac{k_{-1} + k_2}{k_1\mathrm{S_t}}\right) + [\mathrm{EA}] = \\ = [\mathrm{EA}]\left(1 + \frac{k_3}{k_2} + \frac{k_3}{k_2} \times \frac{k_{-1} + k_2}{k_1\mathrm{S_t}}\right) = \\ = [\mathrm{EA}]\left(\frac{k_1k_2\mathrm{S_t} + k_1k_3\mathrm{S_t} + k_{-1}k_3 + k_2k_3}{k_1k_2\mathrm{S_t}}\right)\end{aligned}$$

Hence

$$[\mathrm{EA}] = \frac{k_1k_2\mathrm{S_t}}{k_1k_2\mathrm{S_t} + k_1k_3\mathrm{S_t} + k_{-1}k_3 + k_2k_3}\mathrm{E_t}$$

And

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2k_3\mathrm{S_t}}{k_1k_2\mathrm{S_t} + k_1k_3\mathrm{S_t} + k_{-1}k_3 + k_2k_3}\mathrm{E_t} = \frac{\frac{k_2k_3}{k_2 + k_3}\mathrm{S_tE_t}}{\frac{k_3(k_{-1} + k_2)}{k_1(k_2 + k_3)} + \mathrm{S_t}}$$

3-5. $v = \frac{k_2k_4\mathrm{E_tGl_tFc_t^+}}{k_4K_{\mathrm{M}}^{\mathrm{Gl}}\mathrm{Fc_t^+} + k_2K_{\mathrm{M}}^{\mathrm{Fc}}\mathrm{Gl_t} + (k_2+k_4)\mathrm{Gl_tFc_t^+}}$; $K_{\mathrm{M}}^{\mathrm{Fc}} = \frac{k_4+k_{-3}}{k_3}$ and $K_{\mathrm{M}}^{\mathrm{Gl}} = \frac{k_2+k_{-1}}{k_1}$.

3-6. Mass balance $E_t = [E]+[CI]+[CII]$; SSAs:

$$0 \sim d[\mathrm{CI}]/dt = k_1[\mathrm{E}][\mathrm{P}] - k_2[\mathrm{CI}][\mathrm{S}]$$

$$0 \sim d[\mathrm{CII}]/dt = k_2[\mathrm{CI}][\mathrm{S}] - k_3[\mathrm{CII}][\mathrm{S}]$$

Three equations, three unknowns. Find expressions for [CI] and [CII] because

$$d[\mathrm{P}]/dt = k_2[\mathrm{CI}][\mathrm{S}] + k_3[\mathrm{CII}][\mathrm{S}]$$

Using the mass balance equations, one obtains

$$\mathrm{E_t} = [\mathrm{CI}]\left(1 + \frac{k_2}{k_3} + \frac{k_2\mathrm{S_t}}{k_1[\mathrm{P}]}\right) = [\mathrm{CI}]\left(\frac{k_1k_2[\mathrm{P}] + k_1k_3[\mathrm{P}] + k_2k_3\mathrm{S_t}}{k_1k_3[\mathrm{P}]}\right)$$

Hence

$$[\mathrm{CI}] = \frac{k_1k_3[\mathrm{P}]\mathrm{E_t}}{k_1k_2[\mathrm{P}] + k_1k_3[\mathrm{P}] + k_2k_3\mathrm{S_t}}$$

and

$$[\mathrm{CII}] = \frac{k_1k_2[\mathrm{P}]\mathrm{E_t}}{k_1k_2[\mathrm{P}] + k_1k_3[\mathrm{P}] + k_2k_3\mathrm{S_t}}$$

Finally

$$\frac{d[\mathrm{P}]}{dt} = \frac{2k_1k_2k_3[\mathrm{P}]\mathrm{E_t}\mathrm{S_t}}{k_1k_2[\mathrm{P}] + k_1k_3[\mathrm{P}] + k_2k_3\mathrm{S_t}}$$

3-7. The expression for k_{obs} in this case is:

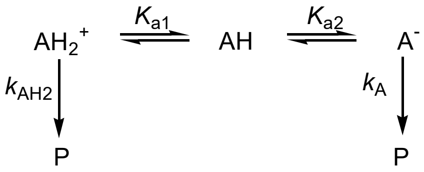
$$k_{\mathrm{obs}} = \frac{k_{\mathrm{AH}}K_{\mathrm{a1}}[\mathrm{H^+}]}{[\mathrm{H^+}]^2 + K_{\mathrm{a1}}[\mathrm{H^+}] + K_{\mathrm{a1}}K_{\mathrm{a2}}}$$

The horizontal part of the curve, when k_{obs} is pH independent, is given by

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{AH}}K_{\mathrm{a1}}[\mathrm{H^+}]}{K_{\mathrm{a1}}[\mathrm{H^+}]} = k_{\mathrm{AH}}$$

Left and right straight lines are given by: $k_{\mathrm{obs}} = \frac{k_{\mathrm{AH}}K_{\mathrm{a1}}[\mathrm{H^+}]}{[\mathrm{H^+}]^2} = \frac{k_{\mathrm{AH}}K_{\mathrm{a1}}}{[\mathrm{H^+}]}$ and $k_{\mathrm{obs}} = \frac{k_{\mathrm{AH}}K_{\mathrm{a1}}[\mathrm{H^+}]}{K_{\mathrm{a1}}K_{\mathrm{a2}}} = \frac{k_{\mathrm{AH}}[\mathrm{H^+}]}{K_{\mathrm{a2}}}$, respectively. Correspondingly, $\log k_{\mathrm{obs}} = \log k_{\mathrm{AH}}$; $\log k_{\mathrm{obs}} = \log k_{\mathrm{AH}} - \mathrm{p}K_{\mathrm{a1}} + \mathrm{pH}$ and $\log k_{\mathrm{obs}} = \log k_{\mathrm{AH}} - \mathrm{pH} + \mathrm{p}K_{\mathrm{a2}}$ for the three straight lines. The values of $\log k_{\mathrm{obs}}$ are equal at the intersections points. This leads to $\mathrm{p}K_{\mathrm{a1}} = \mathrm{pH}$ and $\mathrm{p}K_{\mathrm{a2}} = \mathrm{pH}$.

3-8. The corresponding scheme is:



Mass balance:

$$A_t = [AH_2^+] + [AH] + [A^-];$$

$$K_{a1} = [AH][H^+]/[AH_2^+];\ \ K_{a2} = [A^-][H^+]/[AH]$$

Substitution affords

$$\mathrm{A_t} = [\mathrm{AH}]\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{a1}}}\right) + [\mathrm{A^-}] = \frac{[\mathrm{A^-}][\mathrm{H^+}]}{K_{\mathrm{a2}}}\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{a1}}}\right) + [\mathrm{A^-}] =$$
$$= [\mathrm{A^-}]\left(1 + \frac{[\mathrm{H^+}]}{K_{\mathrm{a2}}} + \frac{[\mathrm{H^+}]^2}{K_{\mathrm{a1}}K_{\mathrm{a2}}}\right)$$

Equilibrium concentrations are

$$[\mathrm{A^-}] = \frac{K_{\mathrm{a1}}K_{\mathrm{a2}}}{[\mathrm{H^+}]^2 + K_{\mathrm{a1}}[\mathrm{H^+}] + K_{\mathrm{a1}}K_{\mathrm{a2}}}\mathrm{A_t}$$

$$[\mathrm{AH_2^+}] = \frac{[\mathrm{H^+}]^2}{[\mathrm{H^+}]^2 + K_{\mathrm{a1}}[\mathrm{H^+}] + K_{\mathrm{a1}}K_{\mathrm{a2}}}\ \mathrm{A_t}$$

Since $d[\mathrm{P}]/dt = k_{\mathrm{A}}[\mathrm{A^-}] + k_{\mathrm{AH2}}[\mathrm{AH_2^+}]$

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{AH2}}[\mathrm{H^+}]^2 + k_{\mathrm{A}}K_{\mathrm{a1}}K_{\mathrm{a2}}}{[\mathrm{H^+}]^2 + K_{\mathrm{a1}}[\mathrm{H^+}] + K_{\mathrm{a1}}K_{\mathrm{a2}}}$$

3-10. The time corresponding to the inflection point is found from the equation $\frac{d^2x}{dt^2} = 0$. The solution of the corresponding equation affords $t = \frac{ln\,(^{a}/_{c})}{k(a+c)}$. Assuming that $A = (a + c)$, one obtains $\frac{dx}{dt} = \frac{acA^2ke^{-Akt}}{\left(c+ae^{-Akt}\right)^2}$. The slope of the straight line when $t = \frac{\ln\,(^{a}/_{c})}{k(a+c)}$, i.e. after substitution of this expression for t into $\frac{dx}{dt}$ gives:

$$\frac{dx}{dt}=\frac{acA^2ke^{-Akt}}{(c+ae^{-Akt})^2}=\frac{acA^2ke^{-\frac{Ak\ln\left(^{a}/_{c}\right)}{Ak}}}{\left(c+ae^{-\ln\left(^{a}/_{c}\right)}\right)^2}=\frac{c^2A^2k}{(c+c)^2}=\frac{A^2k}{4}=\alpha$$

Check that the units of α are {M s^{-1}}, cf. with "slope". The value of x ("y" at y axis) at $t=\frac{\ln\left(^{a}/_{c}\right)}{k(a+c)}$ is

$$"y"=\frac{ac\left(1-\frac{c}{a}\right)}{2c}=\frac{a-c}{2}$$

The equation for the straight line $y = \alpha t + \beta$ passing through the inflection point is

$$\frac{a-c}{2}=\frac{A^2k}{4}\times\frac{\ln\left(^{a}/_{c}\right)}{k(a+c)}+\beta$$

This allows to find β as

$$\beta=\frac{2(a-c)-A\ln\left(^{a}/_{c}\right)}{4}$$

Using this expression one can find time τ, at which "y" equals zero

$$0=\frac{A^2k}{4}\tau+\frac{2(a-c)-A\ln\left(^{a}/_{c}\right)}{4}\quad\text{and}\quad\tau A^2k=A\ln\left(^{a}/_{c}\right)-2(a-c)$$

Finally

$$\tau=\frac{\ln\left(^{a}/_{c}\right)-2\frac{a-c}{a+c}}{k(a+c)}$$

3-12. Show that the following mechanism works, if both rapidly established equilibria are strongly shifted to the left.[1]

$$\text{phenol}\rightleftharpoons\text{phenoxide}^-+H^+$$

$$\text{phenoxide}^-+Os^{III}\rightleftharpoons\text{phenoxyl}^\bullet+Os^{II}$$

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[1] Adapted from Song N, Stanbury DM, *Inorg Chem*, **2012**, *51*, 4909.

$$2\ \text{phenoxyl}^{\bullet} \rightarrow \text{biphenoquinone}$$

3-13. Lineweaver-Burk: $v^{-1} = V_M^{-1} + K_M/(V_M[S])$. When $v^{-1} = 0$, $[S] = -K_M$.

3-14. The Michaelis-Menten equation in a linear form is

$$vK_M + v[S] = V_M[S]$$

After dividing both sides by [S] and rearrangement one arrives to

$$v = V_M - K_M v[S]^{-1}$$

The slope and intercept of a linear v vs. $v[S]^{-1}$ plot equal $-K_M$ and V_M, respectively.

3-15. $y = 0$ when $[S_0] = [S]$. Then $0 = V_M - K_M/t$ and $t = K_M/V_M$.

4-1. $E_t = [E] + [ES] + [ES']$; $K_s = [E][S]/[ES]$; $K'_s = [E][S]/[ES']$; $E_t = [E_S]\{K_s/[S] + 1 + (K_s/[S])\times([S]/K'_s)\}$ and hence $[ES] = E_t[S]K'_s/\{K_sK'_s + [S](K_s + K'_s)$; $v = k[ES]$. Substitution of the expression for [ES] into the equation for v affords

$$v = \frac{k\dfrac{K_s'}{K_s + K_s'}[S][E]}{\dfrac{K_sK_s'}{K_s + K_s'} + [S]}$$

4.2. In this case $v = k[ES] + k'[ES_2]$. $[ES] = E_t[S]/\{K_s + [S] + [S]^2/K_{2s}\}$ (see footnote to page 4-2). $E_t = [ES_2]\{(K_S/[S])\times(K_{2S}/[S]) + K_{2S}/[S] + 1\}$; $[ES_2] = E_t\{[S]^2\times K_{2S}^{-1}/[K_S + [S] + [S]^2\times K_{2S}^{-1}]\}$. Correspondingly

$$v = \frac{k[S] + k'\dfrac{[S]^2}{K_{2S}}}{K_S + [S] + \dfrac{[S]^2}{K_{2S}}}E_t$$

When [S] is relatively small and the term $[S]^2\times K_{2S}^{-1}$ is negligible, $v \sim kE_t$. When [S] is large, $v \sim k'E_t$. Therefore the rate will never drop at high [S], if $k' > k$.

4-3. The noncompetitive inhibition.

4.4. In this case

$$v = \frac{k_{\text{cat}} \dfrac{K_{\text{i}}}{K_{\text{i}} + [\text{I}]} \text{E}_{\text{t}}[\text{S}]}{K_{\text{s}} + [\text{S}]}$$

At [I] = $i_{0.5}$ v = ½v, i.e.

$$\frac{1}{2}v = \frac{k_{\text{cat}} \dfrac{K_{\text{i}}}{K_{\text{i}} + [i_{0.5}]} \text{E}_{\text{t}}[\text{S}]}{K_{\text{s}} + [\text{S}]}$$

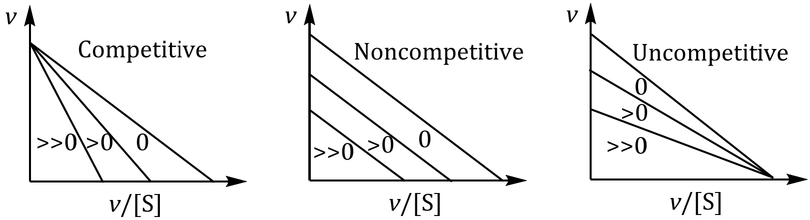
Without inhibition

$$v = \frac{k_{\text{cat}}\text{E}_{\text{t}}[\text{S}]}{K_{\text{s}} + [\text{S}]}$$

Dividing the latter by the former affords

$$2 = \frac{K_{\text{i}} + [i_{0.5}]}{K_{\text{i}}}$$

4-5.



5.1. Under the steady-state conditions (see problem 3-2 when $k_{-\text{I}} \approx 0$)

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2[\text{oxidant}][\text{S}]}{k_1[\text{oxidant}] + k_2[\text{S}]}\text{C}_{\text{t}}$$

One should find the condition when all Rc is rapidly and quantitatively converted to Ac, i.e. the overall rate is determined by k_2 only. This occurs when k_1[oxidant] >> k_2[S] because in this case

$$\frac{d[\text{P}]}{dt} \approx \frac{k_1 k_2[\text{oxidant}][\text{S}]}{k_1[\text{oxidant}]}\text{C}_{\text{t}} = k_2[\text{oxidant}][\text{S}]\text{C}_{\text{t}}$$

5-2. It comes from eq 5.2.4 that

$$\frac{\mathrm{S_t}}{\mathrm{S_t} - x_\infty} = e^{\frac{k_{\mathrm{II}}}{k_{\mathrm{i}}}\mathrm{C_t}}$$

Therefore

$$x_\infty = \mathrm{S_t}(1 - e^{-\frac{k_{\mathrm{II}}}{k_{\mathrm{i}}}\mathrm{C_t}})$$

See ref. 3 in Lecture 5 for details.

6-2. Since $\frac{\partial lnk}{\partial p} = -\frac{\Delta V^{\neq}}{RT}$, a two-fold increase in the rate constant means $\partial lnk = \Delta lnk = ln2k - lnk = ln2$. This corresponds to Δp, which should be found. Substitution the numerical values into the right part of the above equation ($T = 298$ K, $R = 82$ cm^3 atm K^{-1} mol^{-1}) gives $\Delta p \sim 1700$ atm.

6-3. Isokinetic relationship means that $\Delta H^{\neq} = \mathrm{T}\Delta S^{\neq}$ + const. After rearrangement $\Delta H^{\neq} - \mathrm{T}\Delta S^{\neq} = \Delta G^{\neq}$ = const, i.e. free energy of activation (and therefore rate constants) is constant within the series.

6-4. The rate expression is given by

$$v = k_1[\mathrm{M}][\mathrm{ROOH}] + k_2[\mathrm{MOH}][\mathrm{ROOH}] + k_3[\mathrm{M}][\mathrm{ROO^-}] + k_4[\mathrm{MOH}][\mathrm{ROO^-}]$$

$$\mathrm{M_t} = [\mathrm{M}] + [\mathrm{MOH}];\ K_{\mathrm{a1}} = \frac{[\mathrm{MOH}][\mathrm{H^+}]}{[\mathrm{M}]};$$

$$\mathrm{ROOH_t} = [\mathrm{ROOH}] + [\mathrm{ROO^-}];\ K_{\mathrm{a2}} = \frac{[\mathrm{ROO^-}][\mathrm{H^+}]}{[\mathrm{ROOH}]}$$

After finding equilibrium concentrations of all four participants followed by substitution into the expression for v, one obtains

$$v = \frac{k_1[\mathrm{H^+}]^2 + k_2K_{\mathrm{a1}}[\mathrm{H^+}] + k_3K_{\mathrm{a2}}[\mathrm{H^+}] + k_4K_{\mathrm{a1}}K_{\mathrm{a2}}}{[\mathrm{H^+}]^2 + K_{\mathrm{a1}}[\mathrm{H^+}] + K_{\mathrm{a2}}[\mathrm{H^+}] + K_{\mathrm{a1}}K_{\mathrm{a2}}}$$

Kinetically indistinguishable are the k_2 and k_3 pathways.

7-1. Mass balance: $\mathrm{MeCHO_t} \approx [\mathrm{MeCHO}]$ (aldehyde is difficult to deprotonate).

$$v = k_2[\mathrm{MeCHO}][^-\mathrm{H_2CCHO}].$$

SSA:

$$0 = k_1[\mathrm{MeCHO}][\mathrm{OH}^-] - [^-\mathrm{H_2CCHO}](k_{-1} + k_2[\mathrm{MeCHO}]).$$

Therefore

$$[^-\mathrm{H_2CCHO}] = k_2[\mathrm{MeCHO}][\mathrm{OH}^-]/(k_{-1} + k_2[\mathrm{MeCHO}]).$$

Correspondingly

$$v = k_1k_2[\mathrm{MeCHO}]^2][\mathrm{OH}^-]/(k_{-1} + k_2[\mathrm{MeCHO}]).$$

This is eq 7.2.1 with k = k_1k_2/k_{-1}, if $k_{-1} >> k_2[\mathrm{MeCHO}]$.

7-2. A) If the last step is fast, the mass balance equation is $\mathrm{Co_t} = [\mathrm{A}] + [\mathrm{B}]$ (A and B are $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ and $[\mathrm{Co(NH_3)_4(NH_2)Cl}]^+$, respectively). SSA for B is

$$0 = k_1[\mathrm{A}][\mathrm{OH}^-] - (k_{-1} + k_2)[\mathrm{B}]$$

Correspondingly

$$[\mathrm{B}] = \frac{k_1[\mathrm{OH}^-]}{k_{-1} + k_2 + k_1[\mathrm{OH}^-]}\mathrm{Co_t}$$

Finally

$$k_{\mathrm{obs}} = \frac{k_1k_2[\mathrm{OH}^-]}{k_{-1} + k_2 + k_1[\mathrm{OH}^-]}$$

because $v = k_2[\mathrm{B}]$.

B) If the last step (k_3) is not fast, the mass balance is $\mathrm{Co_t} = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]$ ($\mathrm{C} = [\mathrm{Co(NH_3)_4(NH_2)}]^{2+}$). SSA should be applied for both B and C:

$$0 = k_1[\mathrm{A}][\mathrm{OH}^-] + k_{-2}[\mathrm{C}][\mathrm{Cl}^-] - (k_{-1} + k_2)[\mathrm{B}]$$

and

$$0 = k_2[\mathrm{B}] - [\mathrm{C}](k_{-2}[\mathrm{Cl}^-] + k_3)$$

The rate is this case is $v = k_3[\mathrm{C}]$. There are three equations with three unknowns. This allows to find the expression for the steady-state concentration of C. Substitution of thus found C into the equation for *v* gives

$$k_{\text{obs}} = \frac{k_1k_2k_3[\text{OH}^-]}{k_1(k_2+k_3)[\text{OH}^-] + k_1k_{-2}[\text{OH}^-][\text{Cl}^-] + k_{-1}k_{-2}[\text{Cl}^-] + (k_{-1}+k_2)k_3}$$

7-3. A) BH $\leftrightharpoons$ B^- + H^+ (K_a); $B_t = BH + B^-$; $[B^-] = K_aB_t/([H^+] + K_a)$. SSA with respect to intermediate **7.1**:

$$0 = (k_1[\text{S}][\text{B}^-] - (k_{-1}+k_2)[\mathbf{7.1}]$$

S_t = [S] + [**7.1**], but since [**7.1**] is very low, $S_t \sim [S]$ and [**7.1**] = $\frac{k_1}{k_{-1}+k_2}\text{S}_\text{t}[\text{B}^-] = \frac{k_1}{k_{-1}+k_2} \times \frac{K_\text{a}}{[\text{H}^+]+K_\text{a}}\text{S}_\text{t}\text{B}_\text{t}$. Correspondingly

$$k_{\text{obs}} = \frac{k_1k_2}{k_{-1}+k_2} \times \frac{K_\text{a}}{[\text{H}^+]+K_\text{a}}\text{B}_\text{t}$$

7-4. Example of a general acid catalysis with $H_2PO_4^-$ as a reactive species.

7-5. Rate ~ $[OH^-]^{-1}$.

8-3. $c_{\text{red}}/c_{\text{ox}} = 0.01$.

8-4. Let us find the conditions when the first derivative is zero. Rearrangement of eq 8.3.1 gives

$$\frac{\lambda}{4}\left(1 + \frac{2\Delta G}{\lambda} + \frac{\Delta G^2}{\lambda^2}\right) = \frac{\lambda}{4} + \frac{\Delta G}{2} + \frac{\Delta G^2}{4\lambda}$$

After differentiation with respect to ΔG gives

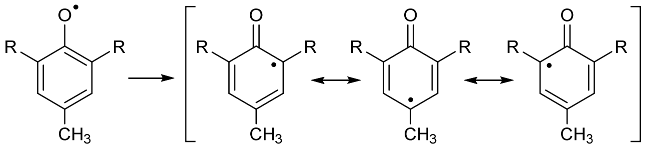
$$0 = \frac{1}{2} + \frac{\Delta G}{2\lambda}$$

And finally, $\lambda = -\Delta G$.

9-1. Inverse rate dependence in $[\text{Co}^{\text{II}}]$.

9-3. The last step in Scheme 9.4.6 should not be fast; rates of steps 2 and 3 should be comparable.

9-4.



9-5. Radical species are potentially carcinogenic.

11-5. Fe−N, Fe−S and Fe−O, respectively.

14-1. Dissociative - S_N1; associative S_N2.

14-4. *S*-Character of the rate versus [Glucose] dependence, which is emphasized in the inset, is indicative of the allosteric regulation of the enzymatic activity by glucose.

14-5. Retention which is due to two inversions.

LECTURE 1.

KEY DEFINITIONS

1.1. A Reaction Mechanism. What Is It?

The most gorgeous in chemistry is almost certainly the understanding of mechanisms of chemical reactions. After finding a novel chemical transformation or synthesizing a new unique compound, the next question that arises inevitably is: "How? How does this reaction occur? Why and how are old bonds cleaved and new bonds are formed?” Apparently, there are certain approaches to study reaction mechanisms. Our ultimate goal is to understand and remember two important issues. First, one should have a clear perception what is the mechanism of a chemical reaction and, second, what methods should be applied for its elucidation in order to claim with confidence that the mechanism of a particular reaction is more or less reliably established.

There are two key definitions.

Definition 1. A mechanism of any chemical reaction is a series of its elementary steps.

Definition 2. A step is referred to as elementary (concerted or synchronous), if it *does not* involve any intermediate.

They define the exact essence of a concept of *a chemical mechanism*. There are two levels of understanding a mechanism. They referred to as *stoichiometric* and *intimate* mechanisms. Note that a stoichiometric mechanism is not synonym of a stoichiometric equation. A stoichiometric mechanism is just a sequence of its elementary steps without detailing the nature of bonds that are cleaved and formed, the nature of orbitals involved, stereochemical features, etc. If these issues are known, one may speak about the intimate mechanism. Consider the electrophilic bromination of ethene. This is an *Ad*$_E$ (addition electrophilic) process. Its stoichiometric *equation* (not stoichiometric mechanism!) is given by eq 1.1.1.

$$H_2C{=}CH_2 + Br_2 \rightarrow H_2CBr{-}CH_2Br \qquad (1.1.1)$$

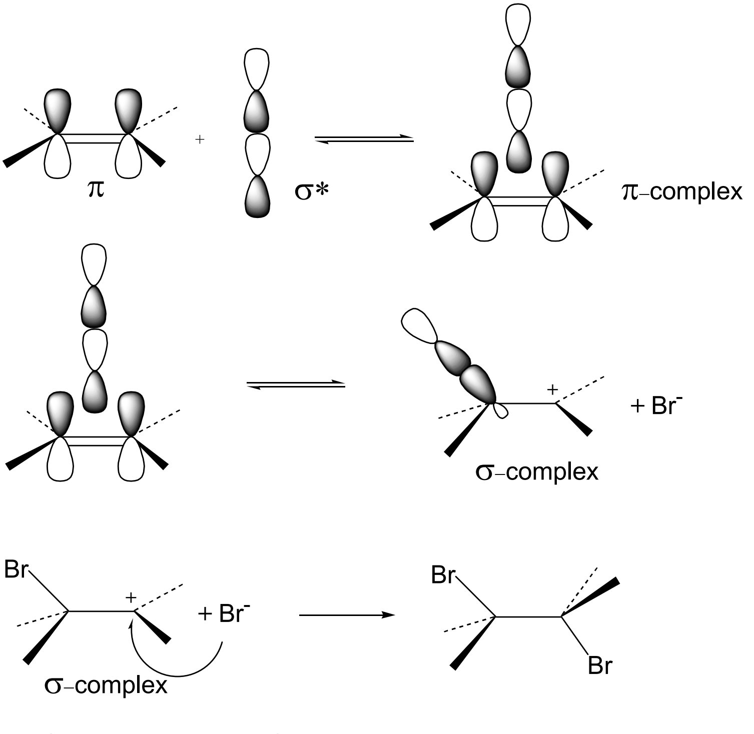
The stoichiometric *mechanism* of reaction 1.1.1 consists of three steps:

$$H_2C{=}CH_2 + Br_2 \rightleftarrows \pi\text{-complex } \{H_2C{=}CH_2, Br_2\} \qquad (1.1.2)$$

$$\pi\text{-complex} \rightleftarrows \sigma\text{-complex } \{Br{-}CH_2{-}CH_2^+\} + Br^- \qquad (1.1.3)$$

$$H_2CBr{-}CH_2^+ + Br^- \rightarrow H_2CBr{-}CH_2Br \qquad (1.1.4)$$

The intimate mechanism of reaction 1.1.1 specifies key molecular orbitals involved and adds stereochemical details:



The information required for establishing a reaction mechanism is the following: