

ϕ_f also defined as

$$\frac{\text{\# of fluorescence photons}}{\text{\# of photons absorbed}}$$

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$$\frac{1}{I_f} = \frac{1}{k_a[S_0]} \left[1 + \frac{k_{ic} + k_{isc}^s}{k_f} \right] + \frac{k_q(Q)}{k_a[S_0]k_f}$$

if $\phi_f \rightarrow 1$, so that $k_f \gg k_{ic}$, $k_f \gg k_{isc}^s$, then

I_f is measured as function of $[Q]$

usually given relative to I_f^0 (without Q)

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f} [Q], \quad I_f^0 = k_a[S_0]\phi_f$$

(with $\phi_f \approx 1$, where $\phi_f = k_f \tau_f$)

Transp. Stern - Volmer plot $\frac{I_f^0}{I_f}$ vs $[Q]$
slope = $\frac{k_q}{k_f}$

Measurement of τ_f X

before continuous illumination was assumed

often easier is use of a short light pulse

if pulsetime short as compared to S_1 decay rate,
then $I_f(t)$ shows directly the decay of S_1

pulses as short as 4 fs ($4 \cdot 10^{-15}$ s) possible

\rightarrow excitation in times much shorter than the
 S_1 decay

after excitation in short time, $[S_1]$ will be smaller
than its SSA value

$$I_f = k_c$$

Inspection of the last two factors in E relationship:

$$k_f \tau_f = \frac{1}{k_f + k_{ic} +}$$

The product of the fluorescence rate const: the radiative rate constant divided by the st to the decay of S_1 . In effect, S_1 decay can ratio of rate constants contained in Equati yield for fluorescence Φ_f , similar to th Section 35.8. The fluorescence quantum y. emitted as fluorescence divided by the n this definition to Equation (36.165) demo will be large for molecules in which k_f is s corresponding to S_1 decay. Inverting Equa the following expression is obtained:

$$\frac{1}{I_f} = \frac{1}{k_a[S_0]} \left(1 + \frac{k}{}$$

For a fluorophore with a quantum yield ap rescence quenching experiments, fluoresc [Q]. Measurements are generally perform sity observed in the absence of quencher I

$$\frac{I_f^0}{I_f} = 1$$

Equation (36.167) reveals that a plot of the [Q] will yield a straight line, with slope c **Stern–Volmer plots**, an example of which

36.9.3 Measurement of τ_f

In the development presented in the pre system of interest was subjected to con approximation could be applied to $[S_1]$. E to excite the system with a temporally sho temporal duration of the pulse is short co this state can be measured directly by mo tion of time. Optical pulses as short as 4 fs excitation on a timescale that is significant

After excitation by a temporally short in $[S_1]$ will be finite. In addition, the rate c

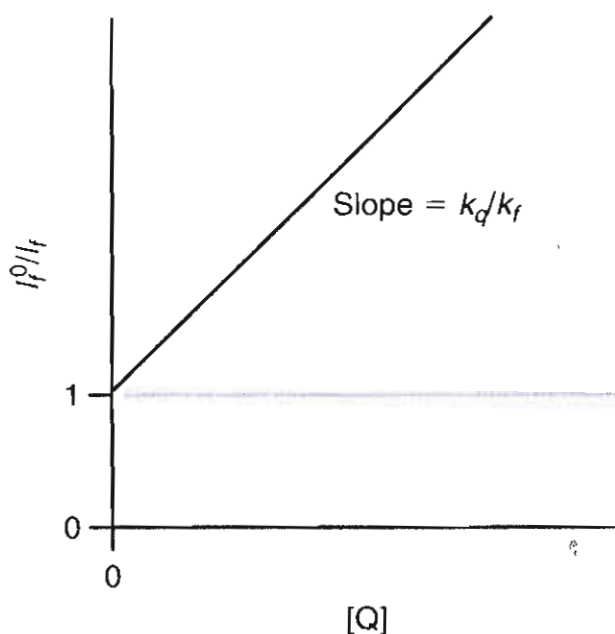


FIGURE 36.19

A Stern–Volmer plot. Intensity of fluorescence as a function of quencher concentration is plotted relative to the intensity in the absence of quencher. The slope of the line provides a measure of the quenching rate constant relative to the rate constant for fluorescence.

further: rate constant for absorption
is $k_a \approx 0$

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$$\rightarrow \frac{d[S_1]}{dt} = -(k_f + k_{ic} + k_{isc}^s + k_q[Q])[S_1]$$

$$= -\frac{[S_1]}{\tau_f}$$

$$\int_{[S_1]_0}^{[S_1]} \frac{d[S_1]}{[S_1]} = -\frac{1}{\tau_f} \int_0^t dt \rightarrow \ln \frac{[S_1]}{[S_1]_0} = -\frac{t}{\tau_f}$$

$$[S_1] = [S_1]_0 e^{-t/\tau_f}$$

$I_f \sim [S_1]$ decays exponentially with time constant τ_f

when $k_f \gg k_{ic}$ and $k_f \gg k_{isc}^s$

then $\frac{1}{\tau_f} \approx k_f + k_q[Q]$

$$\lim_{k_f \gg k_{ic}, k_{isc}^s} \tau_f = \frac{1}{k_f + k_q[Q]}$$

→ measurement of fluorescence lifetime at
known quencher concentration $[Q]$ + slope
of a Stern-Volmer plot

enough to determine k_f and k_q
reciprocal equation:

$$\frac{1}{\tau_f} = k_f + k_q[Q]$$

$\frac{1}{\tau_f}$ vs $[Q]$ → straight line with slope = k_q and

intercept = k_f

fluorescence of pyrene in solution
with C_6Br_6 as quencher:

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$[C_6Br_6]$ (mM)	0.5	1.0	2.0	3.0	5.0
τ_f (s)	$2.66 \cdot 10^{-7}$	$1.87 \cdot 10^{-7}$	$1.17 \cdot 10^{-7}$	$8.50 \cdot 10^{-8}$	$5.51 \cdot 10^{-8}$
τ_f (ns)	266 ns	187 ns	117 ns	85 ns	55 ns
k_f, k_q ?					

plot data as $\frac{1}{\tau_f}$ vs $[C_6Br_6]$

Transparency plot

linear regression fit (e.g. like with Excel in Lab)

$$\rightarrow \text{slope} = 3.00 \cdot 10^9 \text{ s}^{-1} = k_q = 3.00 \cdot 10^9 \frac{1}{10^9 \text{ ns}} = 3.00 \text{ ns}^{-1}$$

$$\text{intercept} = 1.98 \cdot 10^6 \text{ s}^{-1} = k_f = 1.98 \cdot 10^6 \frac{1}{10^6 \mu\text{s}} = 1.98 \mu\text{s}^{-1}$$

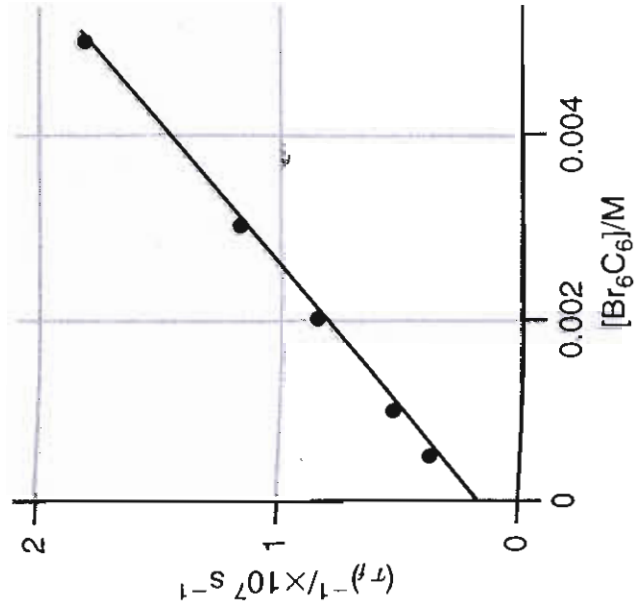
$$\frac{1}{\tau_f} = k_f + k_q [Q]$$

Q4 Tuesday 9.12.2014

0.0005	2.66×10^{-7}
0.001	1.87×10^{-7}
0.002	1.17×10^{-7}
0.003	8.50×10^{-8}
0.005	5.51×10^{-8}

Solution

Using Equation (36.171), a plot of $(\tau_f)^{-1}$ versus [Q] for this system is as follows:



The best fit to the data by a straight line corresponds to a slope of $3.00 \times 10^9 \text{ s}^{-1}$, which is equal to k_q by Equation (36.171), and a y intercept of $1.98 \times 10^6 \text{ s}^{-1}$, which is equal to k_f .

- Photochemical Processes

~~Catalysis~~ - Review 36

= Chemical Change involved

if that happens in excited state S_1 , then the process is just another branch of S_1 decay
photochemical rate:

$$R_{\text{Photochem.}} = k_{\text{Photochem.}}^S [S_1]$$

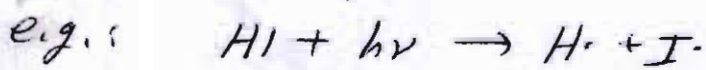
but the photochem. process can also happen through the excited triplet state T_1 :

$$\rightarrow R_{\text{Photochem.}} = k_{\text{Photochem.}}^T [T_1]$$

for many photochemical processes 1 photon is not enough to start a chemical reaction
overall quantum yields:

$$\phi = \frac{\# \text{ of reactants consumed in time } t}{\# \text{ of photons absorbed in same time } t}$$

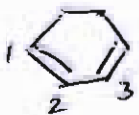
$\phi > 1$ is also possible



1 photon absorbed \rightarrow 2HI consumed

$$\rightarrow \phi = 2$$

1,3 cyclohexadiene + $h\nu \rightarrow$ cis hexatriene



all π bonds
cis

found in experiment:

(35)-2

2.5 mmol 1,3-cyclohexadiene are converted to cis-hexatriene in 27.0 s of irradiation with 100. W (Watt = $\frac{J}{s}$) of 280. nm light when all light is absorbed by the sample for conversion, what is ϕ total photon energy absorbed:

$$E_{abs} = \text{Power} \cdot \Delta t = 100. \frac{J}{s} \cdot 27.0 s = 2.70 \text{ kJ}$$

Photon energy:

$$E_{phot} = h\nu = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} \text{ J s} \cdot 2.998 \cdot 10^8 \frac{m}{s}}{2.80 \cdot 10^{-7} m} = 7.10 \cdot 10^{-19} \text{ J}$$

no. of photons absorbed:

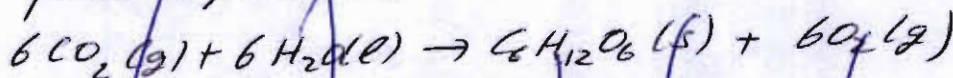
$$N_{phot} = \frac{E_{abs}}{E_{phot}} = \frac{2.70 \cdot 10^3 \text{ J}}{7.10 \cdot 10^{-19} \text{ J}} = 3.80 \cdot 10^{21}$$

no. of moles of photons (einstein):

$$n_{phot} = \frac{3.80 \cdot 10^{21}}{N_A} = \frac{3.80 \cdot 10^{21}}{6.022 \cdot 10^{23}} = 6.31 \cdot 10^{-3} \text{ einstein}$$

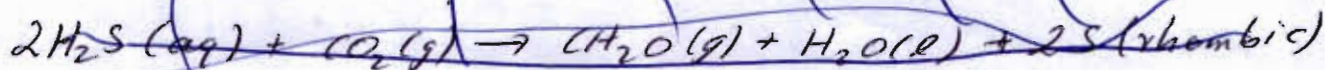
$$\phi = \frac{2.50 \cdot 10^{-3} \text{ mol (reacted)}}{6.31 \cdot 10^{-3} \text{ mol (photons absorbed)}} = 0.396 \approx 0.40$$

biology: photo synthesis:



$$\Delta G^\circ = +2870 \text{ kJ}$$

in green sulfur bacteria also CO_2 is used, but but with H_2S and CH_2O production, not sugar



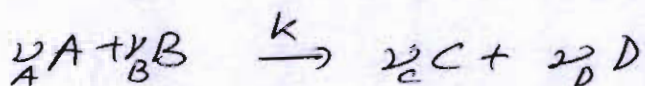
$$\Delta G^\circ = 88 \text{ kJ}$$

C in CO_2 is reduced

O in H_2O / S in H_2S oxidized

$\rightarrow e^-$ transfer (Redox)

setup of rate equations:



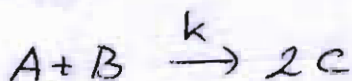
eg. rate of formation of C:

k: product of reactant conc.

$$\frac{1}{\nu_C} \frac{d[C]}{dt} = k [A]^{\nu_A} [B]^{\nu_B} \quad \nu_C > 0 \text{ for products}$$

rate of consumption of A:

$$-\frac{1}{\nu_A} \frac{d[A]}{dt} = k [A]^{\nu_A} [B]^{\nu_B} \quad \nu_A < 0 \text{ for reactants}$$

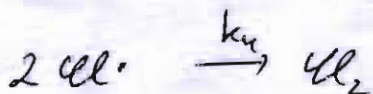
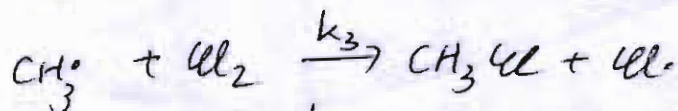
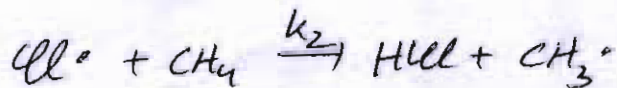
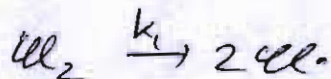


$$\Rightarrow \frac{1}{2} \frac{d[C]}{dt} = k[A][B]$$

$$\Rightarrow \frac{d[C]}{dt} = 2k[A][B]$$

$$-\frac{d[A]}{dt} = k[A][B]$$

mechanism



$$\frac{d[\text{HCl}]}{dt} = k_2 [\text{Cl}\cdot] [\text{CH}_4]$$

↳ intermediate

= formed by k_1 and k_3

consumed by k_2 and k_4

intermediate = no reactant or product

but formed and consumed in the mechanism

$[\text{Cl}\cdot]$ must be eliminated for correct rate eq.

SSA: $\frac{d[\text{Cl}\cdot]}{dt} = 0$ for $\text{CH}_3\cdot$: only in 2 reactions

$$\frac{d[\text{CH}_3\cdot]}{dt} = 0 = +k_2 [\text{Cl}\cdot] [\text{CH}_4] - k_3 [\text{CH}_3\cdot] [\text{Cl}_2]$$

formation \oplus consumption \ominus

$$[\text{CH}_3\cdot] = \frac{k_2 [\text{Cl}\cdot] [\text{CH}_4]}{k_3 [\text{Cl}_2]}$$

for $[\text{Cl}\cdot]$ = SSA:

$$\frac{d[\text{Cl}\cdot]}{dt} = 0 = \underset{\uparrow}{2k_1} [\text{Cl}_2] - k_2 [\text{Cl}\cdot] [\text{CH}_4] + k_3 [\text{CH}_3\cdot] [\text{Cl}_2]$$

2 $\text{Cl}\cdot$ formed in

1 step

$$- 2k_4 [\text{Cl}\cdot]^2$$

2 $\text{Cl}\cdot$ consumed in 1 step

$$0 = 2k_1 [\text{Cl}_2] - k_2 [\text{Cl}\cdot] [\text{CH}_4] + k_3 \frac{k_2 [\text{Cl}\cdot] [\text{CH}_4]}{k_3 [\text{Cl}_2]} [\text{Cl}_2]$$

$$- 2k_4 [\text{Cl}\cdot]^2$$

$$0 = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{CH}_4] + k_3[\text{Cl}\cdot][\text{CH}_3] - 2k_4[\text{Cl}\cdot]^2 \quad (35) - 5$$

$$0 = 2k_1[\text{Cl}_2] - 2k_4[\text{Cl}\cdot]^2$$

$$[\text{Cl}\cdot] = \sqrt{\frac{k_1}{k_4} [\text{Cl}_2]}$$

$$[\text{CH}_3\cdot] = \frac{k_2 \sqrt{\frac{k_1}{k_4} [\text{Cl}_2]} [\text{CH}_4]}{k_3 [\text{Cl}_2]}$$

$$\rightarrow R = \frac{d(\text{CHCl}_3)}{dt} = k_2 \sqrt{\frac{k_1}{k_4}} \sqrt{[\text{Cl}_2]} [\text{CH}_4]$$

$\frac{1}{2}$ order in $[\text{Cl}_2]$

1. order in CH_4

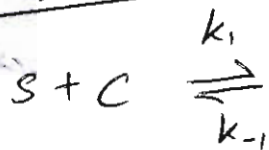
$\frac{3}{2}$ order overall

$$k_{\text{apparent}} = k_2 \sqrt{\frac{k_1}{k_4}}$$

$$R = \frac{k[A]}{k' + k''[A]} \frac{1}{[B]} \quad \begin{array}{l} -1 \text{ order} \\ \text{in B} \\ \text{no order} \\ \text{in A} \end{array}$$

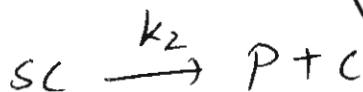
Catalysis

order example



fast equilibrium

$$\Rightarrow K_1 = \frac{k_1}{k_{-1}} = \text{const.}$$



$$\frac{d[P]}{dt} = k_2(SC)$$

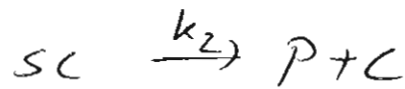
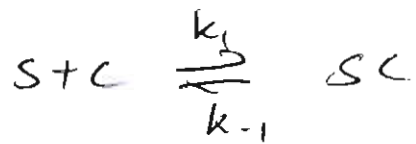
product formation
intermediate

$$K_1 = \frac{[S][C]}{[SC]} \Rightarrow [SC] = \frac{[S][C]}{K_1}$$

$$\rightarrow \frac{d[P]}{dt} = \frac{k_2[S][C]}{K_1}$$

Catalysis

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product formation = $R = \frac{d(P)}{dt} = k_2(SC)$
intermediate

SSA

$$\frac{d(SC)}{dt} = 0 = k_1[S][C] - (k_{-1} + k_2)[SC]$$

$$[SC] = \frac{k_1}{k_{-1} + k_2} [S][C] = \frac{[S][C]}{K_m}$$

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

$$\rightarrow R = \frac{k_2[S][C]}{K_m}$$

into

with $[S]_0 = [S] + [SC] + [P] \Rightarrow [S] =$

$$[C]_0 = [C] + [SC] \Rightarrow [C] =$$

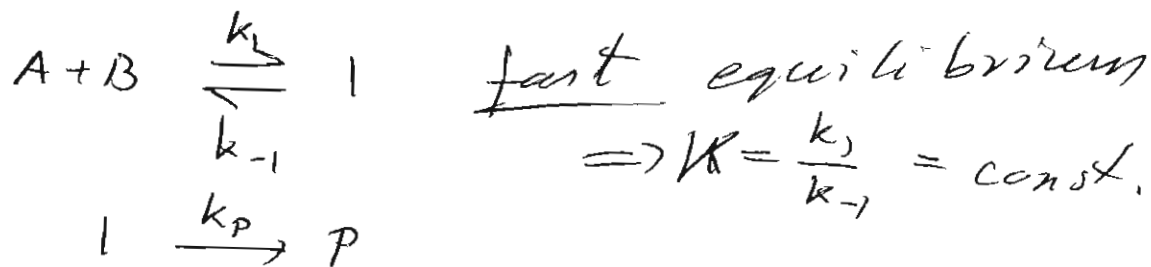
$$\rightarrow [SC] = \frac{[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

near $t=0$

$$\rightarrow R_0 = \frac{k_2[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

Pre-equilibrium

(35) - 7



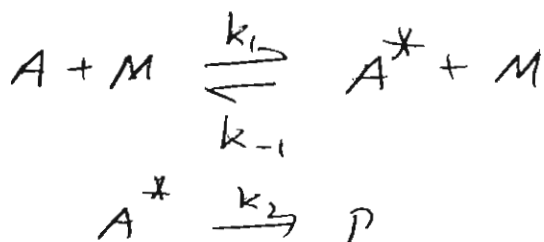
$$R = \frac{d(P)}{dt} = k_p [I] \quad \text{intermediate}$$

$$K = \frac{[I]}{[A][B]}$$

$$\rightarrow [I] = K[A][B]$$

$$\rightarrow R = \frac{d(P)}{dt} = k_p K[A][B]$$

Lindemann



$$\frac{d(P)}{dt} = k_2 [A^*] \quad \text{intermediate}$$

$$\text{SSA} \quad \frac{d(A^*)}{dt} = 0 = k_1 [A][M] - (k_{-1} [M] + k_2) [A^*]$$

$$[A^*] = \frac{k_1 [A][M]}{k_{-1} [M] + k_2} = \frac{k_1 [A]}{k_{-1} + \frac{k_2}{[M]}}$$

$$k_{uni} = \frac{k_1 [M]}{k_{-1} [M] + k_2}$$

$$R = \frac{d[P]}{dt} = \frac{k_1 k_2 [M] (A)}{k_{-1} [M] + k_2}$$

$$= k_{uni} (A)$$

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$

Electron Transfer

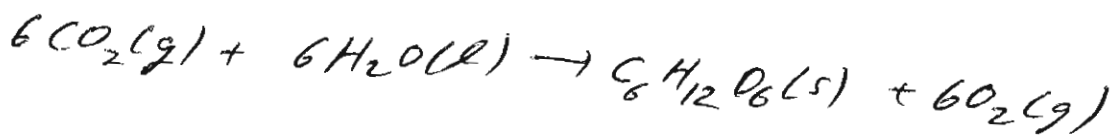
(38) - 1

reactions involving charge exchange between chemicals

especially often in biochem. r.

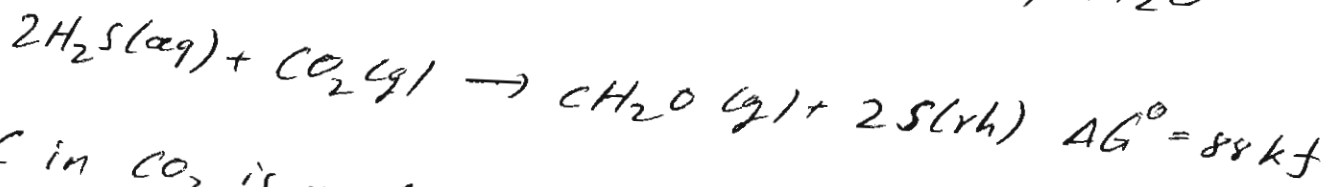
e.g. Photosynthesis

following in plants:



$$\Delta G^\circ = 2870 \text{ kJ}$$

in green sulfur bacteria: H_2S instead of H_2O



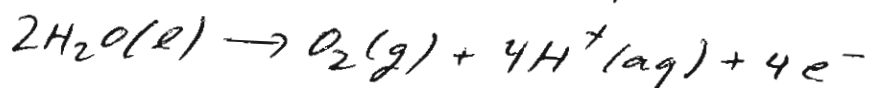
C in CO_2 is reduced

$\text{H}_2\text{O}/\text{H}_2\text{S}$ is oxidized

Photosynthesis many reaction steps involving e^- -transfers

radiation used to transport e^- from two chlorophyll molecules to pheophytin (similar structure as chlorophyll): very fast $\approx 3 \text{ ps}$
 e^- -transfer also pheophytin \rightarrow quinone (200 ps)
then to a second quinone in 100 ps.

quinone electrons used to "split" water:



at the end \rightarrow sugar + O_2

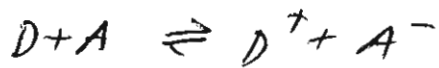
(33) - 2

yields a proton gradient through cell membrane
used to drive ATP synthesis

Simple kinetic model of e^- transfer

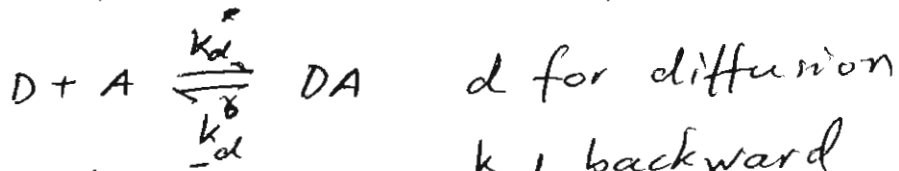
e^- from Donor molecule D to acceptor (A)

$\rightarrow D^+$ (oxidation) + A^- (reduction)



1. D and A form DA complex

diffusion in solution until they are close



e^- transfer in DA complex:



et for electron transfer

k_{-et} for backwards

k_{b-et} in books back-et

then separations



R: rate of formation of products $D^+ + A^-$

$$R = k_{sep} [D^+ A^-]$$

$D^+ A^-$ intermediate \Rightarrow SSA

$$\frac{d[D^+ A^-]}{dt} = 0 = k_{et} [DA] - k_{-et} [D^+ A^-] - k_{sep} [D^+ A^-]$$

$$\Rightarrow [D^+ A^-] = \frac{k_{et} [DA]}{k_{-et} + k_{sep}}$$

k_{-et} = backward et

DA also intermediate \Rightarrow SSA

$$\frac{d(DA)}{dt} \stackrel{SSA}{=} 0 = k_{et}(D)(A) - k_{-et}[D^+A^-] - k_{sep}[D^+A^-]$$

$$[D^+A^-] = \frac{k_{et}}{k_{-et} + k_{sep}} [DA]$$

$$\frac{d(DA)}{dt} = k_d(D)(A) - k_{-d}[DA] - k_{et}[DA] + k_{-et}[D^+A^-] = 0 \text{ (SSA)}$$

$$[DA] = \frac{k_d(D)(A) + k_{-et}[D^+A^-]}{k_{-d} + k_{et}}$$

$$[D^+A^-] = \frac{k_{et}}{k_{-et} + k_{sep}} [DA]$$

$$\frac{k_{-et} + k_{sep}}{k_{et}} [D^+A^-] = \frac{k_d}{k_{-d} + k_{et}} (D)(A) + \frac{k_{-et}}{k_{-d} + k_{et}} [D^+A^-]$$

$$\left[\frac{k_{-et} + k_{sep}}{k_{et}} - \frac{k_{-et}}{k_{-d} + k_{et}} \right] [D^+A^-] = \frac{k_d}{k_{-d} + k_{et}} (D)(A)$$

$$\frac{(k_{-et} + k_{sep})(k_{-d} + k_{et}) - k_{et}k_{-et}}{k_{et}(k_{-d} + k_{et})} [D^+A^-] = \frac{k_d}{k_{-d} + k_{et}} (D)(A)$$

$$[\cdot k_{et}(k_{-d} + k_{et})]$$

$$[(k_{-et} + k_{sep})(k_{-d} + k_{et}) - k_{et}k_{-et}] [D^+A^-] = k_{et}k_d (D)(A)$$

$$(k_{-et} k_{-d} + k_{-et} k_{et} + k_{sep} k_{-d} + k_{sep} k_{et} - k_{-et} k_{et}) \cdot [D^+ A^-] = k_{et} k_d [D] [A]$$

$$(k_{-et} k_{-d} + k_{sep} k_{-d} + k_{sep} k_{et}) [D^+ A^-] = k_{et} k_d [D] [A]$$

$$[D^+ A^-] = \frac{k_{et} k_d}{k_{-et} k_{-d} + k_{sep} k_{-d} + k_{sep} k_{et}} [D] [A]$$

$$R = k_{sep} [D^+ A^-]$$

$$R = \frac{k_{sep} k_{et} k_d}{k_{-et} k_{-d} + k_{sep} k_{-d} + k_{sep} k_{et}} [D] [A]$$

$$= \frac{k_{sep} k_{et} k_d}{(k_{-et} + k_{sep}) k_{-d} + k_{sep} k_{et}} [D] [A]$$

1. order in A and D

if ~~A⁺~~ $D^+ A^-$ dissociation ~~fast~~ much faster than ~~k~~ e^- -back transfer (k_{-et});

$$k_{sep} \gg k_{-et}$$

$$\rightarrow R = \frac{k_{et} k_d k_{sep}}{k_{sep} (k_{-d} + k_{et})} [D] [A] = \frac{k_{et} k_d}{k_{-d} + k_{et}} [D] [A]$$

if in addition

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$k_{et} \gg k_{-d}$ large rate of e^- -transfer
slow complex dissociation

\Rightarrow formation of $D + A$ is rate limiting

but if $k_{-d} \gg k_{et}$

then e^- -transfer is rate limiting?

$$R = \frac{k_{sep} k_{et} k_d}{k_{-et} k_{-d} + k_{sep} (k_{-d} + k_{et})} [D][A]$$

$$\approx \frac{k_{sep} k_{et} k_d}{k_{-et} k_{-d} + k_{sep} k_{-d}} [D][A]$$

$$= \frac{k_d}{k_{-d}} \frac{k_{sep} k_{et}}{k_{-et} + k_{sep}} [D][A]$$

$$K_{d-d} = \frac{k_d}{k_{-d}}$$

equil. constant for $D + A \rightleftharpoons DA$

then farther (before)

$$k_{sep} \gg k_{-et}$$

$$\rightarrow R \approx K_{d-d} k_{et} [D][A]$$

$$= k_{exp} [D][A]$$

important case, if D & A are (33) -6
linked by a covalent bond as in many
biological systems which breaks when D^+A^-
is formed $\rightarrow k_{sep} \gg k_{-d}$

k_{sep} for separation of D^+A^-
into $D^+ + A^-$