Elementary steps and the Molecularity

- Kinetics of the elementary step depends only on the number of reactant molecules in that step!
  - Molecularity → the number of reactant molecules that participate in elementary steps

The Kinetics of Elementary Steps

- For the elementary step

$$A \rightarrow products \qquad v = k[A]$$

  - unimolecular step

- For elementary steps involving more than one reactant

  - a bimolecular step

$$A + B \rightarrow products \quad v = k[A][B]$$

- For the step

$$A + B + C \rightarrow products \qquad \mathrm{v} = \mathrm{k}\left[\mathrm{A}\right]\left[B\right]\left[C\right]$$

  - a termolecular (three molecule) step.
  - Termolecular (and higher) steps are not that common in reaction mechanisms.

Lindemann-Hinshelwood Mechanism

- An early attempt omplex reactions.

Mechanism

$$A + A \xrightarrow{ka} A^*$$

$$A^* + A \xrightarrow{k_a'}$$

$$A^* \xrightarrow{kb} P$$

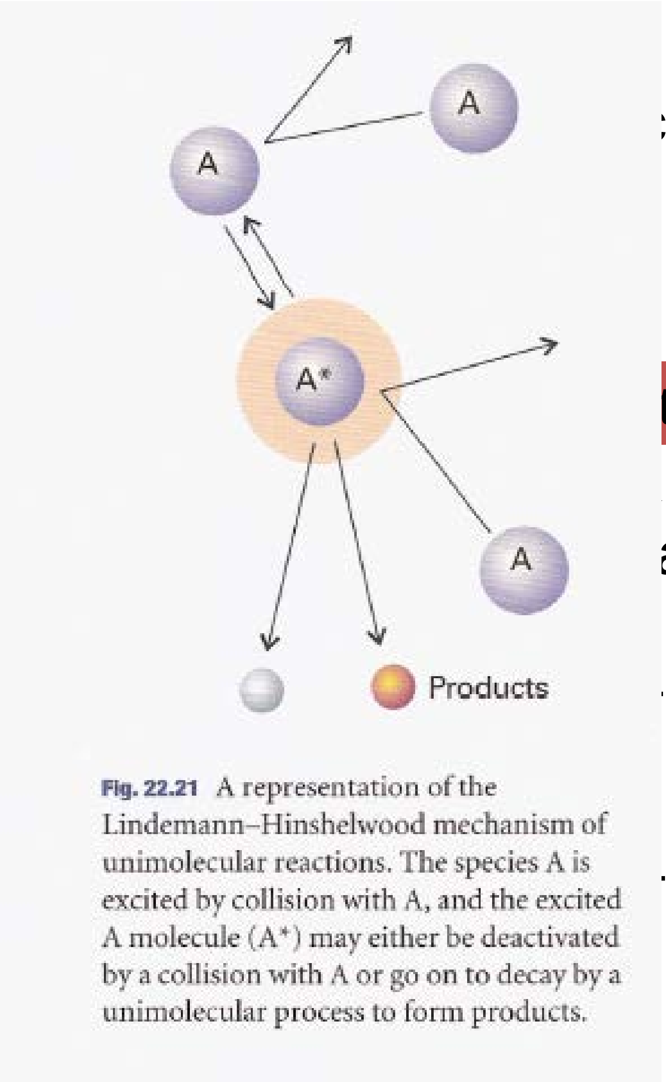


Fig. 22.21 A representation of the Lindemann–Hinshelwood mechanism of unimolecular reactions. The species A is excited by collision with A, and the excited A molecule (A*) may either be deactivated by a collision with A or go on to decay by a unimolecular process to form products.

te Laws

$${}_a[A]^2$$

$$k_a'[A][A^*]$$

$$k_b[A^*]$$

The ‘Activated’ Intermediate

- Formation of the product depends directly on the [A*].
- Apply the SSA to the net rate of formation of the intermediate [A*]

$$\frac{d\left[A^*\right]}{dt} = k_a\left[A\right]^2 - k_a^{'}\left[A^*\right]\left[A\right] - k_b\left[A^*\right] \approx 0$$

Unimolecular reaction

$$A + A \xrightarrow{k_a} A^{*} + A$$

$$A^{*} + A \xrightarrow{k'_a} 2A$$

$$A^{*} \xrightarrow{k_b} P$$

- Substituting and rearranging

$$\frac{d\left[P\right]}{dt} = \frac{k_a k_b \left[A\right]^2}{k_b + k'_a \left[A\right]}$$

The ‘Apparent Rate Constant’ Depends on Pressure

$$A + A \xrightarrow{ka} A^* + A$$

$$A^* + A \xrightarrow{k_a'} 2A$$

$$A^* \xrightarrow{k_b} P$$

$$\frac{d[P]}{dt} = \frac{k_a k_b [A]^2}{k_b + k_a' [A]}$$

The rate laws for the Lindemann-Hinshelwood Mechanism are pressure dependent.

High Pressure Case

$$k_b << k_a'[A]$$

$$\frac{d[P]}{dt} = \frac{k_b k_a [A]}{k_a'}$$

$$= k[A]$$

Low Pressure Case

$$k_b >> k_a'[A]$$

$$\frac{d[P]}{dt} = k_a [A]^2$$

$$= k \ [A]^2$$

The Pressure Dependence of k’

- In the Lindemann-Hinshelwoood Mechanism, the rate constant is pressure dependent.

$$\frac{d\left[P\right]}{dt}=\frac{k_a k_b\left[A\right]^2}{k_b+k_a^{'}\left[A\right]}=k[A]$$

$$\frac{1}{k}=\frac{1}{k_a\left[A\right]}+\frac{k_a^{'}}{k_a k_b}$$

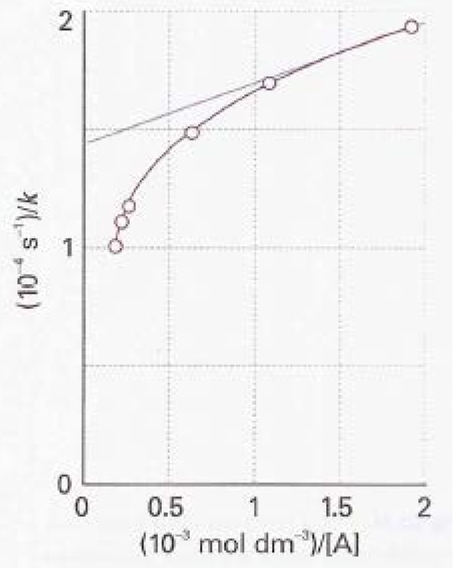


Fig. 22.22 The pressure dependence of the unimolecular isomerization of *trans*-

Unimolecular reaction: example

Example:

$N_2O_5 \rightarrow NO_2 + NO_3$

In chemical kinetics experiments sometimes this reaction looks like a first order reaction and sometimes it looks like a second order reaction, depending on the reaction conditions. For example, you might change the apparent order of the reaction by changing the pressure.

The postulated mechanism is:

$$N_2O_5 + N_2O_5 \overset{k_2}{\rightleftarrows} N_2O_5^* + N_2O_5$$

$$N_2O_5^* \overset{k_1}{\rightarrow} NO_2 + NO_3$$

the formation of products is a unimolecular process which has a rate law of

$$\frac{d[NO_2]}{dt} = k_1[N_2O_5^*]$$

The activated N_2O_5 (that is, the $N_2O_5\cdot$) is a transient species because it is neither a reactant nor a product. It is produced during the course of the reaction and it is gone at the end of the reaction.

Unimolecular reaction: example

Rate of change of the concentration of the transient is,

$$\frac{d[\mathrm{N_2O_5}^*]}{dt} = k_2[\mathrm{N_2O_5}]^2 - k_{-2}[\mathrm{N_2O_5}][\mathrm{N_2O_5}^*] - k_1[\mathrm{N_2O_5}^*] \qquad . \qquad (5)$$

Set of coupled first order differential equations in time: can be solved exactly. But the **steady state approximation** will allow us to obtain a simple, but approximate, solution.

$$\frac{d[\mathrm{N_2O_5}^*]}{dt} \approx 0$$

$$k_2[\mathrm{N_2O_5}]^2 - k_{-2}[\mathrm{N_2O_5}][\mathrm{N_2O_5}^*] - k_1[\mathrm{N_2O_5}^*] = 0$$

$$[\mathrm{N_2O_5}^*] = \frac{k_2[\mathrm{N_2O_5}]^2}{k_1 + k_{-2}[\mathrm{N_2O_5}]}$$

$$\frac{d[\mathrm{NO_2}]}{dt} = k_1[\mathrm{N_2O_5}^*] \qquad \text{Rate} = k_1[\mathrm{N_2O_5}^*] = \frac{k_1 k_2[\mathrm{N_2O_5}]^2}{k_1 + k_{-2}[\mathrm{N_2O_5}]}$$

We now must ask whether or not this rate law fits the experimental fact that sometimes the reaction appears to be first order in N_2O_5 and sometimes it appears to be second order in N_2O_5.

Unimolecular reaction: example

$$N_2O_5 + N_2O_5 \overset{k_2}{\rightleftarrows} N_2O_5^* + N_2O_5$$

$$N_2O_5^* \xrightarrow{k_1} NO_2 + NO_3$$

If $k_1 >> k_{-2}\,[N_2O_5]$, that is, when $[N_2O_5]$ is small, then the

Rate $\approx k_2[N_2O_5]^2$

and the reaction looks like it is second order.

If $k_1 << k_{-2}\,[N_2O_5]$, that is, when $[N_2O_5]$ is large, then the

$$\text{Rate} \approx \frac{k_1 k_2}{k_{-2}}[N_2O_5]$$

and the reaction looks like it is first order.

Unimolecular reaction: example

Variation of Lindemann mechanism: an inert gas, M, is present.
The proposed mechanism is:

$$\mathrm{A} + \mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{A}^* + \mathrm{A}$$

$$\mathrm{A} + \mathrm{M} \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_1} \mathrm{B} + \mathrm{C}$$

The rate is $$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}^*]$$

But for the transient species $$\frac{d[\mathrm{A}^*]}{dt} = k_2[\mathrm{A}]^2 - k_{-2}[\mathrm{A}][\mathrm{A}^*] + k'_2[\mathrm{A}][\mathrm{M}] - k'_{-2}[\mathrm{A}^*][\mathrm{M}] - k_1[\mathrm{A}^*] \approx 0$$

Using the steady state approximation we solve for [A*]

$$[\mathrm{A}^*] = \frac{k_2[\mathrm{A}]^2 + k'_2[\mathrm{A}][\mathrm{M}]}{k_1 + k_{-2}[\mathrm{A}] + k'_{-2}[\mathrm{M}]}$$

Unimolecular reaction: example

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}^*] \quad \text{and} \quad [\mathrm{A}^*] = \frac{k_2[\mathrm{A}]^2 + k'_2[\mathrm{A}][\mathrm{M}]}{k_1 + k_{-2}[\mathrm{A}] + k'_{-2}[\mathrm{M}]}$$

$$\mathrm{Rate} = k_1[\mathrm{A}^*] = k_1 \frac{k_2[\mathrm{A}]^2 + k'_2[\mathrm{A}][\mathrm{M}]}{k_1 + k_{-2}[\mathrm{A}] + k'_{-2}[\mathrm{M}]}$$

If [M] = 0 then we are back to the Lindemann mechanism. However, there are new possibilities.
If we make [M] very large, large enough to overwhelm all the other terms in the rate law, the effective rate law becomes,

$$\mathrm{Rate} \rightarrow k_1 \frac{k'_2[\mathrm{A}][\mathrm{M}]}{k'_{-2}[\mathrm{M}]} = \frac{k_1 k'_2}{k'_{-2}}[\mathrm{A}]$$

That is, the reaction becomes effectively first order in A independent of the values of either [A] or [M] (as long as [M] is large).

Unimolecular reaction: example

Sometimes the conditions are such that there is virtually no "self activation" of the A molecules and all of the activation comes from collisions of A molecules with the inert gas molecules, M. Our mechanism covers this case. We can obtain the rate law in this case by setting k_2 and k_{-2} equal to zero. This gives

$$\text{Rate} = \frac{d[\mathrm{B}]}{dt} = k_1 \frac{k'_2[\mathrm{A}][\mathrm{M}]}{k_1 + k'_{-2}[\mathrm{M}]}$$

the reaction is first order in A regardless of the M concentration, but the actual reaction rate depends on [M]. One can define an effective first order rate constant by rewriting the rate equation as

$$\frac{d[\mathrm{B}]}{dt} = k_1 \frac{k'_2[\mathrm{M}]}{k_1 + k'_{-2}[\mathrm{M}]}[\mathrm{A}]$$

and the effective rate constant is $k_{\mathrm{eff}} = k_1 \dfrac{k'_2[\mathrm{M}]}{k_1 + k'_{-2}[\mathrm{M}]}$

Change the effective first order rate constant, and hence the half-life of the reaction, by adjusting [M].

The rate law may contain species that are not part of the balanced chemical reaction.

Three body reactions:

Example 1: $O\cdot + O\cdot + M \rightarrow O_2 + M$

Example 2: $OH + NO_2 + M \rightarrow HNO_3 + M$

Example 3: $O + O_2 + M \rightarrow O_3 + M$

Three-body reactions

$A + B + M \rightarrow AB + M$

- The three-body reaction actually does not take place as the result of the simultaneous collision of all three molecules A, B, and M. The probability of such an event happening is practically zero.

- What actually occurs is that molecules A and B collide to produce an energetic intermediate AB*.

- In order for AB* to proceed to the product AB, its excess energy must be removed through collision with another molecule denoted by M, to which the excess energy is transferred.

- The third body M is any inert molecule that can remove the excess energy from AB* and eventually dissipate it as heat. (N_2, O_2 in the atmosphere)

$A + B \rightarrow AB^*$

$AB^* \rightarrow A + B$

$AB^* + M \rightarrow AB + M^*$

$M^* \rightarrow M + \text{heat}$

Steady-state approximation (SSA)

- When an intermediate (e.g., AB*) has a very short lifetime and reacts as soon as it is produced, the rate of generation of AB* is equal to the rate of disappearance.

- The excited complex AB* has a very short lifetime and reacts as soon as it is produced. We may therefore assume that it is in steady state at all times

$A + B \rightarrow AB^*$ (k_3)

$AB^* \rightarrow A + B$ (k_4)

$AB^* + M \rightarrow AB + M^*$ (k_5)

$M^* \rightarrow M + \text{heat}$ (k_6)

$$k_3[A][B] = k_4[AB^*] + k_5[AB^*][M]$$

$$\frac{d}{dt}[AB] = k_5[AB^*][M]$$

$$[AB^*] = \frac{k_3[A][B]}{k_4 + k_5[M]}$$

$$\frac{d}{dt}[AB] = \frac{k_3 k_5[A][B][M]}{k_4 + k_5[M]}$$

Product Formation Rate of Three-body Reactions: High and low pressure limit

$$\frac{d}{dt}[AB] = \frac{k_3 k_5 [A][B][M]}{k_4 + k_5 [M]}$$

The formation rate of AB depends on the concentration of M, i.e., pressure-dependent.

(1) Low-pressure limit case:

$k_5[M] << k_4$ → $\frac{d}{dt}[AB] = \frac{k_3 k_5}{k_4}[A][B][M]$

$k_o = k_3 k_5 / k_4$ is referred as the *low-pressure limit rate constant*. Third order reaction

(2) High-pressure limit case:

[M] is sufficiently large → $k_5[M] >> k_4$, → $\frac{d}{dt}[AB] = k_3 [A][B]$

k_3 is referred as the *high-pressure limit rate constant* k_∞. Second order reaction.

Product Formation Rate of Three-body Reactions: General Form

$$\frac{d}{dt}[AB] = \frac{k_0[A][B][M]}{1 + \frac{k_0}{k_\infty}[M]}$$

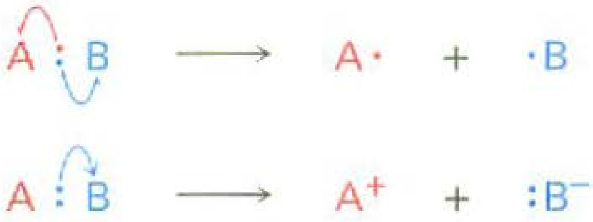
(1) At low pressure, the reaction is a third-order reaction while at high pressure it is a second-order reaction.

(2) The pressure at which the reaction changes from the 3rd order to the 2nd order becomes low with increasing complexity of the product molecule AB.

$H + H + M \rightleftarrows H_2 + M$ is a 3rd order reaction up to 10^4 atm
$OH + NO_2 + M \rightleftarrows HNO_3 + M$ is a 2nd order reaction under tropospheric conditions.

Chain reaction

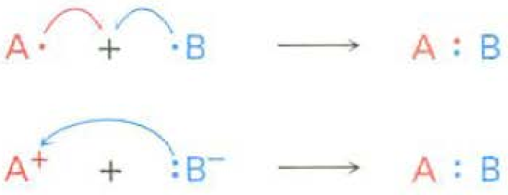
there are two ways in which a covalent two-electron bond can break. A bond can break in an electronically *symmetrical* way so that one electron remains with each product fragment, or a bond can break in an electronically *unsymmetrical* way so that both bonding electrons remain with one product fragment, leaving the other with a vacant orbital. The symmetrical cleavage is said to be *homolytic,* and the unsymmetrical cleavage is said to be *heterolytic*. We'll develop the point in more detail later, but you might note for now that the movement of *one* electron in the symmetrical process is indicated using a half-headed, or "fishhook," arrow (⌒), whereas the movement of *two* electrons in the unsymmetrical process is indicated using a full-headed curved arrow (↷).



Symmetrical bond-breaking (radical):
one bonding electron stays with each product.

Unsymmetrical bond-breaking (polar):
two bonding electrons stay with one product.

Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form. A bond can form in an electronically symmetrical way if one electron is donated to the new bond by each reactant or in an unsymmetrical way if both bonding electrons are donated by one reactant.

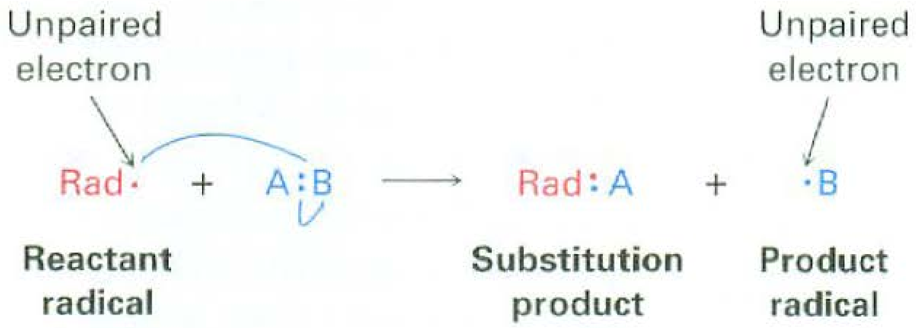


Symmetrical bond-making (radical):
one bonding electron is donated by each reactant.

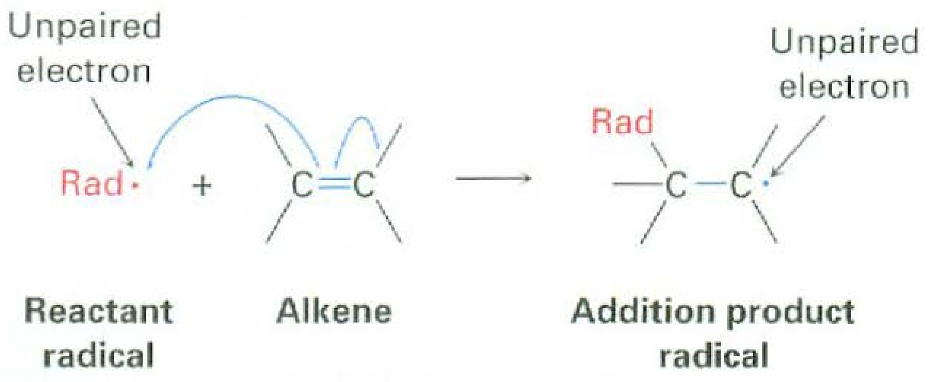
Unsymmetrical bond-making (polar):
two bonding electrons are donated by one reactant.

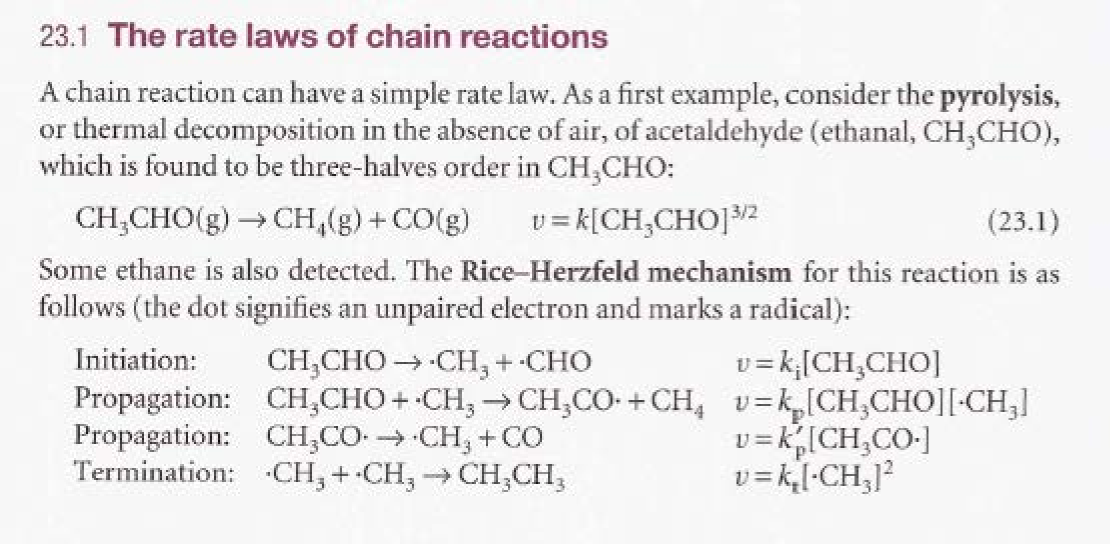
Processes that involve symmetrical bond-breaking and bond-making are called **radical reactions**. A **radical**, often called a *free radical,* is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals. Processes that involve unsymmetrical bond-breaking and bond-making are called **polar reactions**. Polar reactions involve species that have an even number of electrons and thus have only electron pairs in their orbitals. Polar processes are by far the more common reaction type in both organic and biological chemistry, and a large part of this book is devoted to their description.

A radical is highly reactive because it contains an atom with an odd number of electrons (usually seven) in its valence shell, rather than a stable, noble-gas octet. A radical can achieve a valence-shell octet in several ways. For example, the radical might abstract an atom and one bonding electron from another reactant, leaving behind a new radical. The net result is a radical substitution reaction:



Alternatively, a reactant radical might add to a double bond, taking one electron from the double bond and yielding a new radical. The net result is a radical addition reaction:





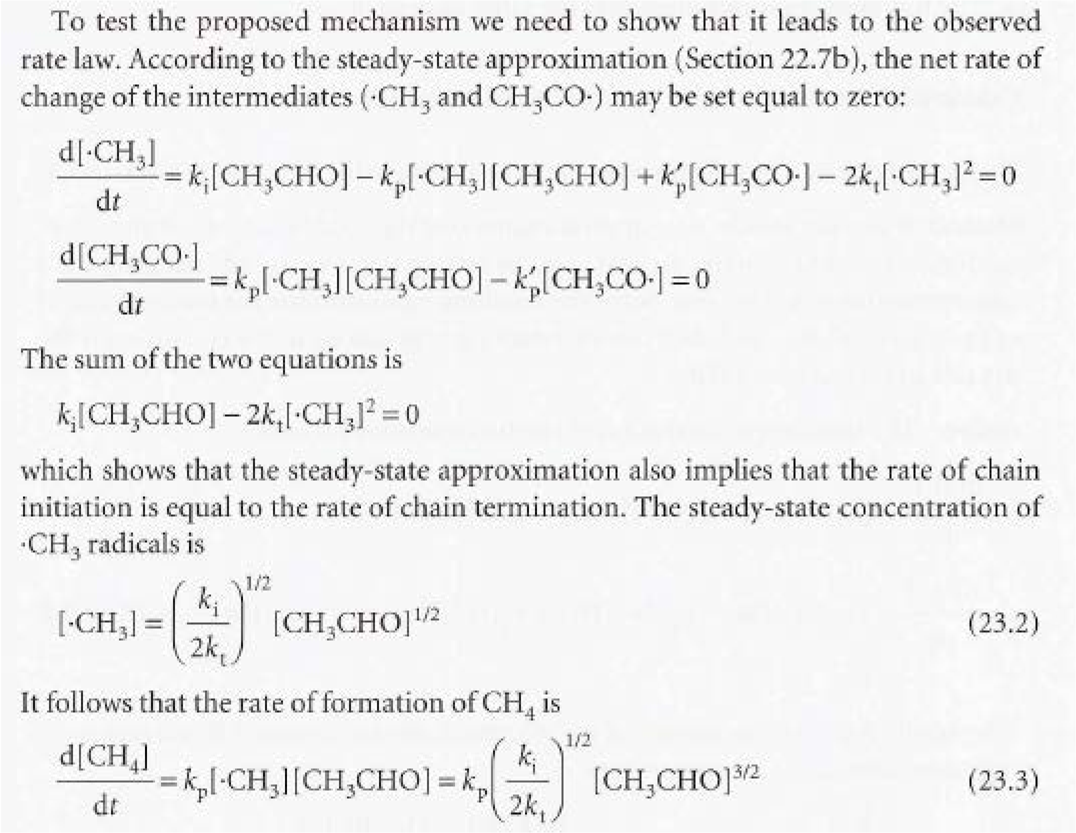
23.1 The rate laws of chain reactions

A chain reaction can have a simple rate law. As a first example, consider the **pyrolysis**, or thermal decomposition in the absence of air, of acetaldehyde (ethanal, CH_3CHO), which is found to be three-halves order in CH_3CHO:

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g) \qquad v = k[CH_3CHO]^{3/2} \tag{23.1}$$

Some ethane is also detected. The **Rice–Herzfeld mechanism** for this reaction is as follows (the dot signifies an unpaired electron and marks a radical):

Initiation:	$CH_3CHO \rightarrow \cdot CH_3 + \cdot CHO$	$v = k_i[CH_3CHO]$
Propagation:	$CH_3CHO + \cdot CH_3 \rightarrow CH_3CO\cdot + CH_4$	$v = k_p[CH_3CHO][\cdot CH_3]$
Propagation:	$CH_3CO\cdot \rightarrow \cdot CH_3 + CO$	$v = k'_p[CH_3CO\cdot]$
Termination:	$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3$	$v = k_t[\cdot CH_3]^2$



To test the proposed mechanism we need to show that it leads to the observed rate law. According to the steady-state approximation (Section 22.7b), the net rate of change of the intermediates ($\cdot CH_3$ and $CH_3CO\cdot$) may be set equal to zero:

$$\frac{d[\cdot CH_3]}{dt} = k_i[CH_3CHO] - k_p[\cdot CH_3][CH_3CHO] + k'_p[CH_3CO\cdot] - 2k_t[\cdot CH_3]^2 = 0$$

$$\frac{d[CH_3CO\cdot]}{dt} = k_p[\cdot CH_3][CH_3CHO] - k'_p[CH_3CO\cdot] = 0$$

The sum of the two equations is

$$k_i[CH_3CHO] - 2k_t[\cdot CH_3]^2 = 0$$

which shows that the steady-state approximation also implies that the rate of chain initiation is equal to the rate of chain termination. The steady-state concentration of $\cdot CH_3$ radicals is

$$[\cdot CH_3] = \left(\frac{k_i}{2k_t}\right)^{1/2} [CH_3CHO]^{1/2} \tag{23.2}$$

It follows that the rate of formation of CH_4 is

$$\frac{d[CH_4]}{dt} = k_p[\cdot CH_3][CH_3CHO] = k_p\left(\frac{k_i}{2k_t}\right)^{1/2} [CH_3CHO]^{3/2} \tag{23.3}$$

In many cases, a chain reaction leads to a complicated rate law. An example is the **hydrogen–bromine reaction**:

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g) \qquad \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \qquad (23.4)$$

The following mechanism has been proposed to account for this rate law (Fig. 23.1):

Initiation: $Br_2 + M \rightarrow Br\cdot + Br\cdot + M \qquad v = k_i[Br_2][M]$

where M is either Br_2 or H_2. This step is an example of a **thermolysis**, a reaction initiated by heat, which stimulates vigorous intermolecular collisions.

Propagation: $Br\cdot + H_2 \rightarrow HBr + H\cdot \qquad v = k_p[Br\cdot][H_2]$

$H\cdot + Br_2 \rightarrow HBr + Br\cdot \qquad v = k'_p[H\cdot][Br_2]$

Retardation: $H\cdot + HBr \rightarrow H_2 + Br\cdot \qquad v = k_r[H\cdot][HBr]$

Termination: $Br\cdot + Br\cdot + M \rightarrow Br_2 + M^* \qquad v = k_t[Br\cdot]^2[M]$

A **retardation step** reduces the net rate of formation of product. In this case, the chain carrier H· attacks a molecule of HBr, the product. In the termination step, the third body M removes the energy of recombination. Other possible termination steps include the recombination of H atoms to form H_2 and combination of H and Br atoms. However, it turns out that only Br atom recombination is important because Br atoms propagate the chain more slowly and thus live longer than H atoms. The net rate of formation of the product HBr is

$$\frac{d[HBr]}{dt} = k_p[Br\cdot][H_2] + k'_p[H\cdot][Br_2] - k_r[H\cdot][HBr]$$

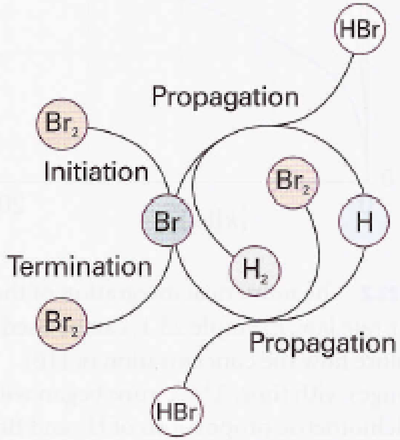


Fig. 23.1 A schematic representation of the mechanism of the reaction between hydrogen and bromine. Note how the reactants and products are shown as arms to the circle, but the intermediates (H and Br) occur only on the circle. Similar diagrams are used to depict the action of catalysts.

Derive the rate law for the formation of HBr according to the mechanism given above.

Method Make the steady-state approximation for the concentrations of any intermediates (H· and Br· in the present case) by setting the net rates of change of their concentrations equal to zero. Solve the resulting equations for the concentrations of the intermediates, and then use the resulting expressions in the equation for the net rate of formation of HBr.

Answer The net rates of formation of the two intermediates are

$$\frac{d[H\cdot]}{dt} = k_p[Br\cdot][H_2] - k'_p[H\cdot][Br_2] - k_r[H\cdot][HBr] = 0$$

$$\frac{d[Br\cdot]}{dt} = 2k_i[Br_2][M] - k_p[Br\cdot][H_2] + k'_p[H\cdot][Br_2] + k_r[H\cdot][HBr] - 2k_t[Br\cdot]^2[M]$$
$$= 0$$

The steady-state concentrations of the intermediates are obtained by solving these two simultaneous equations and are

$$[Br\cdot] = \left(\frac{k_i}{k_t}\right)^{1/2}[Br_2]^{1/2} \qquad [H\cdot] = \frac{k_p(k_i/k_t)^{1/2}[H_2][Br_2]^{1/2}}{k'_p[Br_2] + k_r[HBr]}$$

Note that [M] has cancelled. When we substitute these concentrations into the expression for d[HBr]/d*t*, we obtain

$$\frac{d[HBr]}{dt} = \frac{2k_p(k_i/k_t)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2] + (k_r/k'_p)[HBr]}$$

This equation has the same form as the empirical rate law (eqn 23.4), so the two empirical rate constants can be identified as

$$k = 2k_p\left(\frac{k_i}{k_t}\right)^{1/2} \qquad k' = \frac{k_r}{k'_p}$$

The rate law shows that the reaction slows down as HBr forms, or as the [HBr]/[Br$_2$] ratio increases. This effect occurs because Br$_2$ molecules compete with HBr molecules for H· atoms, with the propagation step H· + Br$_2$ → HBr + Br· yielding product (HBr) and the retardation step H· + HBr → H$_2$ + Br· converting HBr back into reactant (H$_2$). Numerical integration of the rate law with mathematical software shows the predicted time dependence of the concentration of HBr for this mechanism (Fig. 23.2).

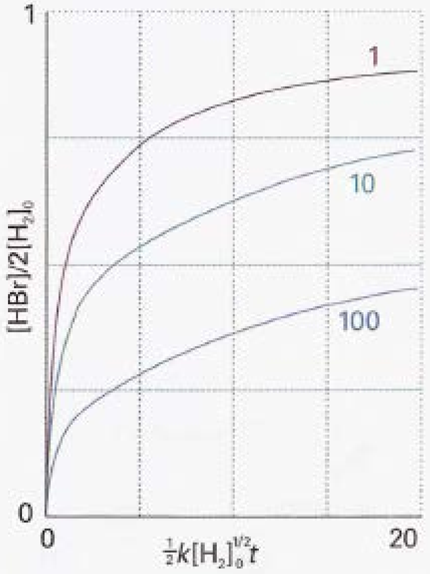


Fig. 23.2 The numerical integration of the HBr rate law, Example 23.1, can be used to explore how the concentration of HBr changes with time. These runs began with stoichiometric proportions of H$_2$ and Br$_2$; the curves are labelled with the value of 2*k*′ – 1.

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Photochemical Processes

In the environment, photochemical reactions have been reported to occur in the **gas phase** (troposphere, stratosphere), **aqueous phase** (atmospheric aerosol or droplets, surface water, land-water interfaces) and in the **solid phase** (plant tissue exteriors, soil and mineral surfaces).

All of these possibilities **need to be taken** into account when fates of organic compounds in nature are considered.

Although in many cases the contribution of photochemical process is **negligible**, in others photolysis is by far the **dominant** pathway for loss of a chemical.

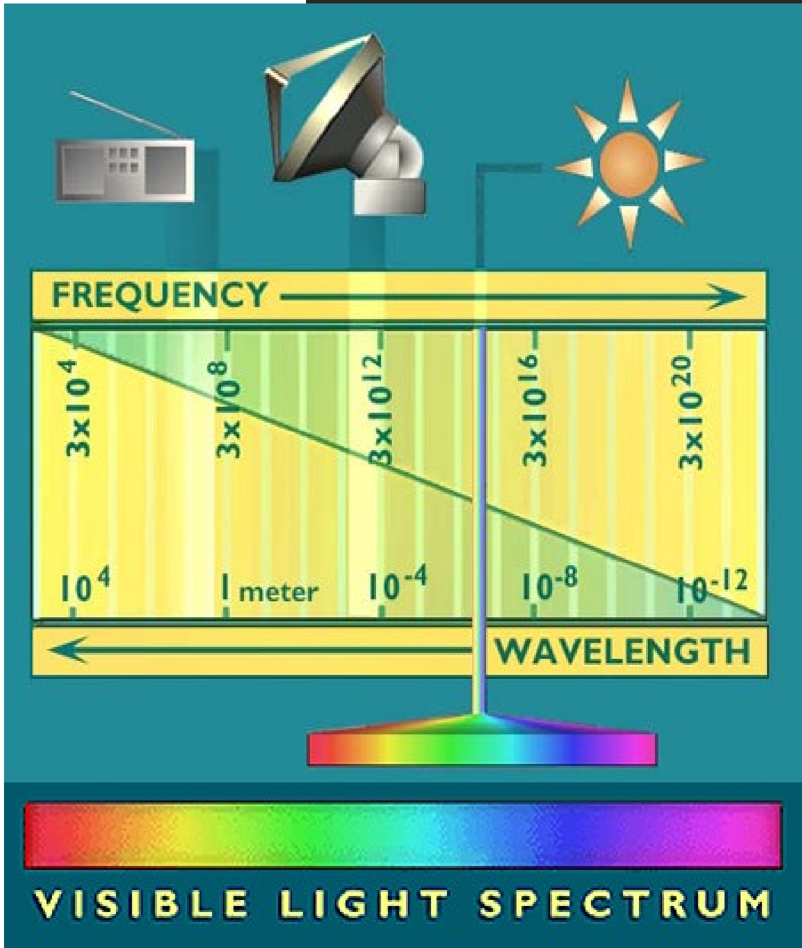
Natural light can induce a variety of processes of environmental importance either directly (when light is absorbed by the species of interest, i.e. fluorescence) or indirectly (when the species of interest reacts with an intermediate called mediator, previously excited or produced by light, i.e. photochemical chain reactions).

Environmentally important phenomena include photosynthesis, photodissociation (e.g., the rupture of organic and inorganic molecules), photoproduction of highly reactive radicals, photodissolution of minerals, photoredox reactions, photochemical smog, etc.

Photochemistry

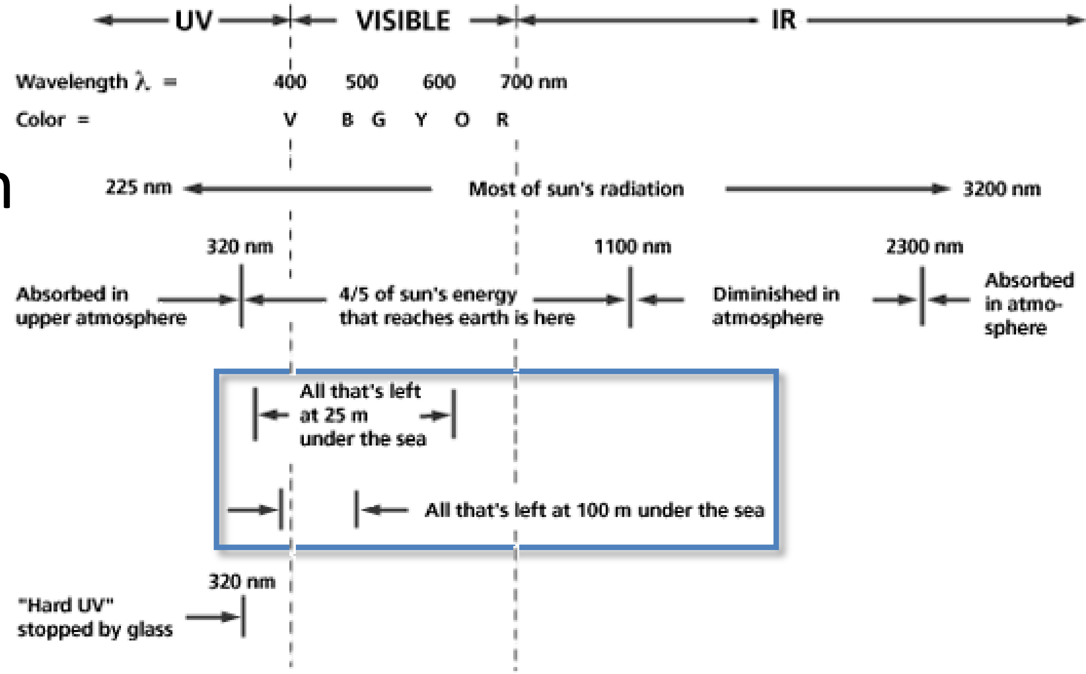
- Sunlight
  - UV, visible, infrared
  - particle-wave duality
    - particle of light = photon
    - 1 mole of photons = 1 einstein (ein)
  - Energy of light
    - $E = N_A h \nu$

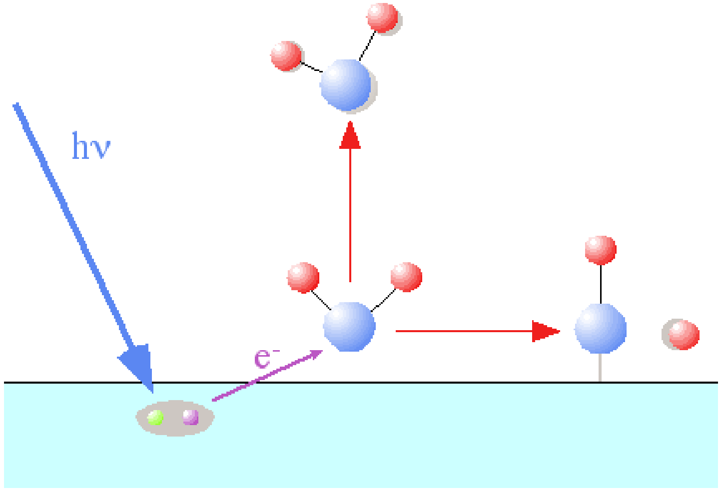
$$E\left(\mathrm{kJ\,ein^{-1}}\right) = \frac{120{,}000}{\lambda\left(\mathrm{nm}\right)}$$



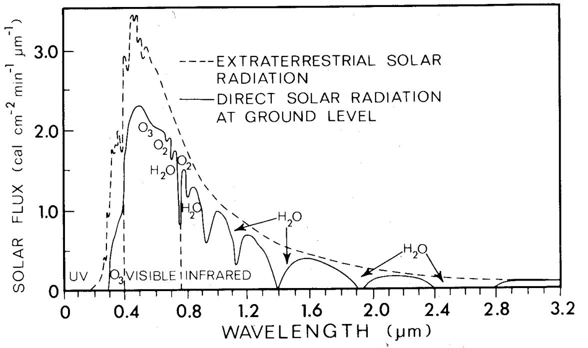
Photochemistry

- Energy of light
  - ultraviolet, 254 nm
    - 470 kJ ein^{-1}
  - violet, 400 nm
    - 300 kJ ein^{-1}
  - red, 700 nm
    - 171 kJ ein^{-1}
  - for comparison: C—C bond strength, 350 kJ mol^{-1}
  - total energy across all wavelengths (λ): 80 kJ min^{-1}





- Excited states
  - A → A*
  - photon absorbed
    → new electronic state / configuration
  - electron promotion to new orbital
    - excited states: singlets and triplets
    - higher potential energy
  - UV-visible light necessary
    to excite molecules
    (higher energy)



Stati di molteplicità

E

S_1

T_1

So

So

So

Stato fondamentale

Stato singoletto

Stato tripletto

vita media di S_1 da 10^{-9} a 10^{-11} sec

vita media di T_1 da 10^{-3} a 10^{1} sec

A

$h\nu$

A*

processi fisici

perdita di energia vibrazionale sotto forma di calore

perdita di energia per emissione di luce (luminescenza)

trasferimento di energia a un'altra molecola (fotosensibilizzazione)

A

reazioni chimiche

frammentazione

riarrangiamento intramolecolare

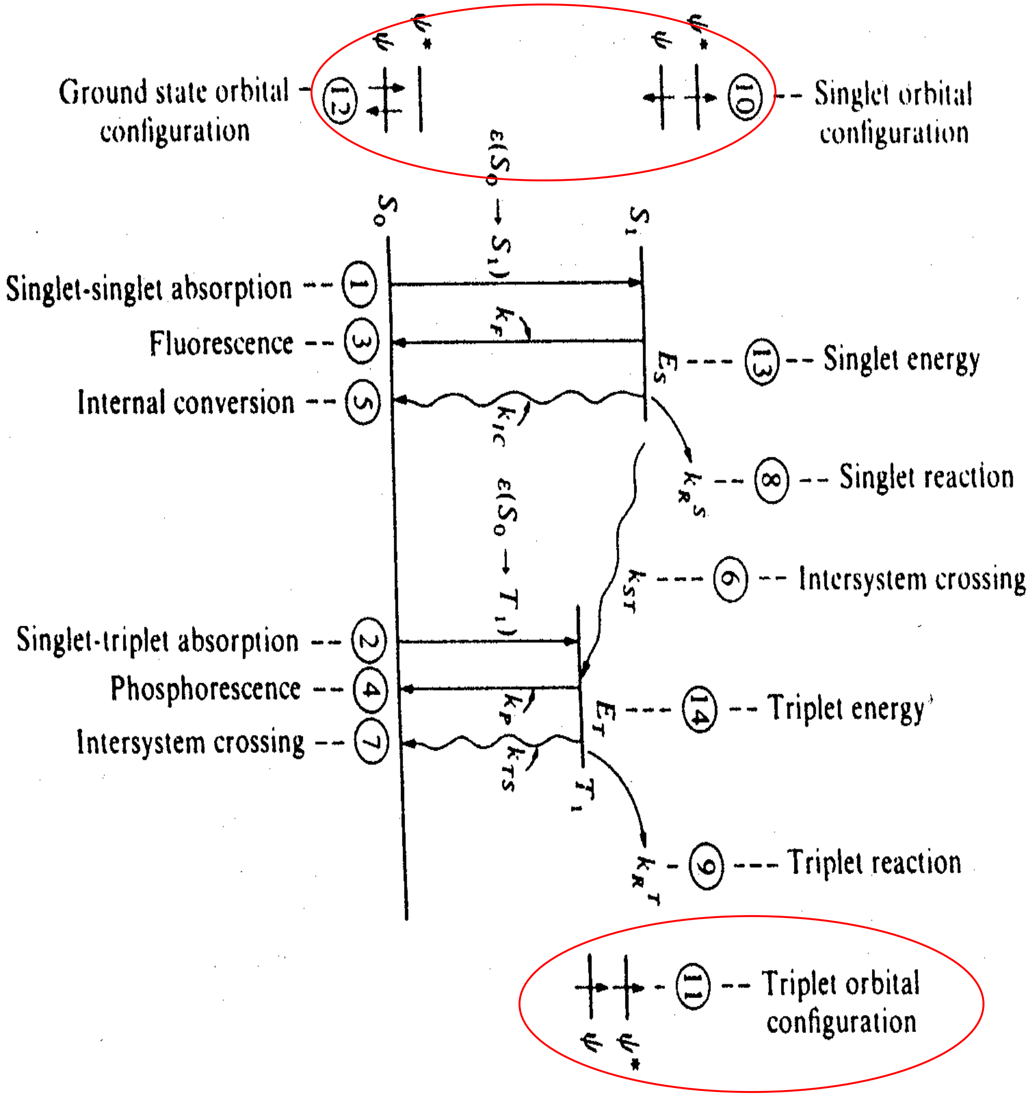
isomerizzazione

dimerizzazione

astrazione di atomo di idrogeno

prodotto(i)

- Singlets, S_0 and S_1
  - spin-paired state
  - short lifetimes
- Triplet, T_1
  - spin-unpaired state
  - longer lifetimes
- Transitions
  - excited to singlets S_1
  - internal conversion
    $S_1 \rightarrow S_0$ + heat
  - fluorescence
    $S_1 \rightarrow S_0 + h\nu$
  - intersystem crossing
    $S_1 \rightarrow T_1$ + heat
  - phosphorescence
    $T_1 \rightarrow S_0 + h\nu$



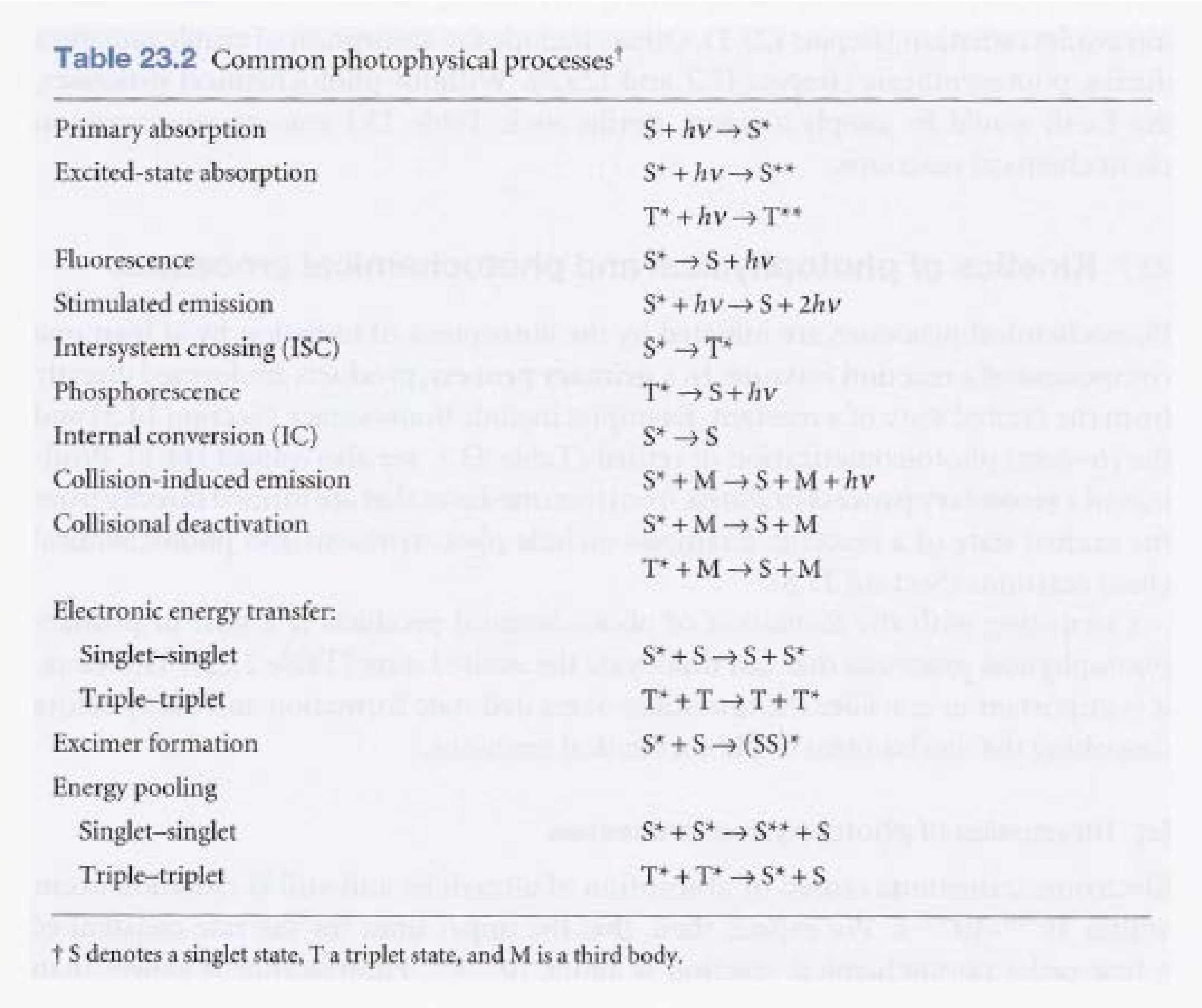
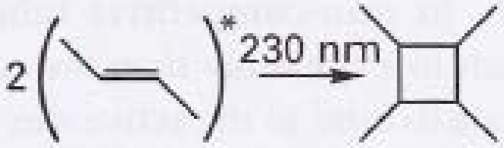
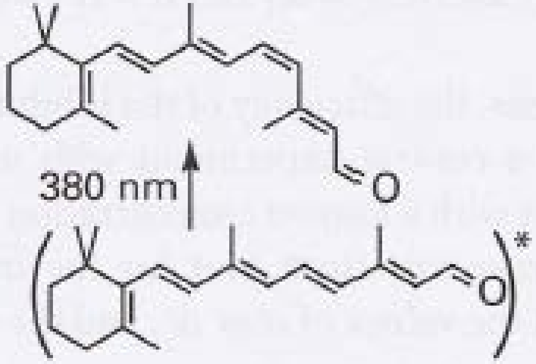


Table 23.2 Common photophysical processes†

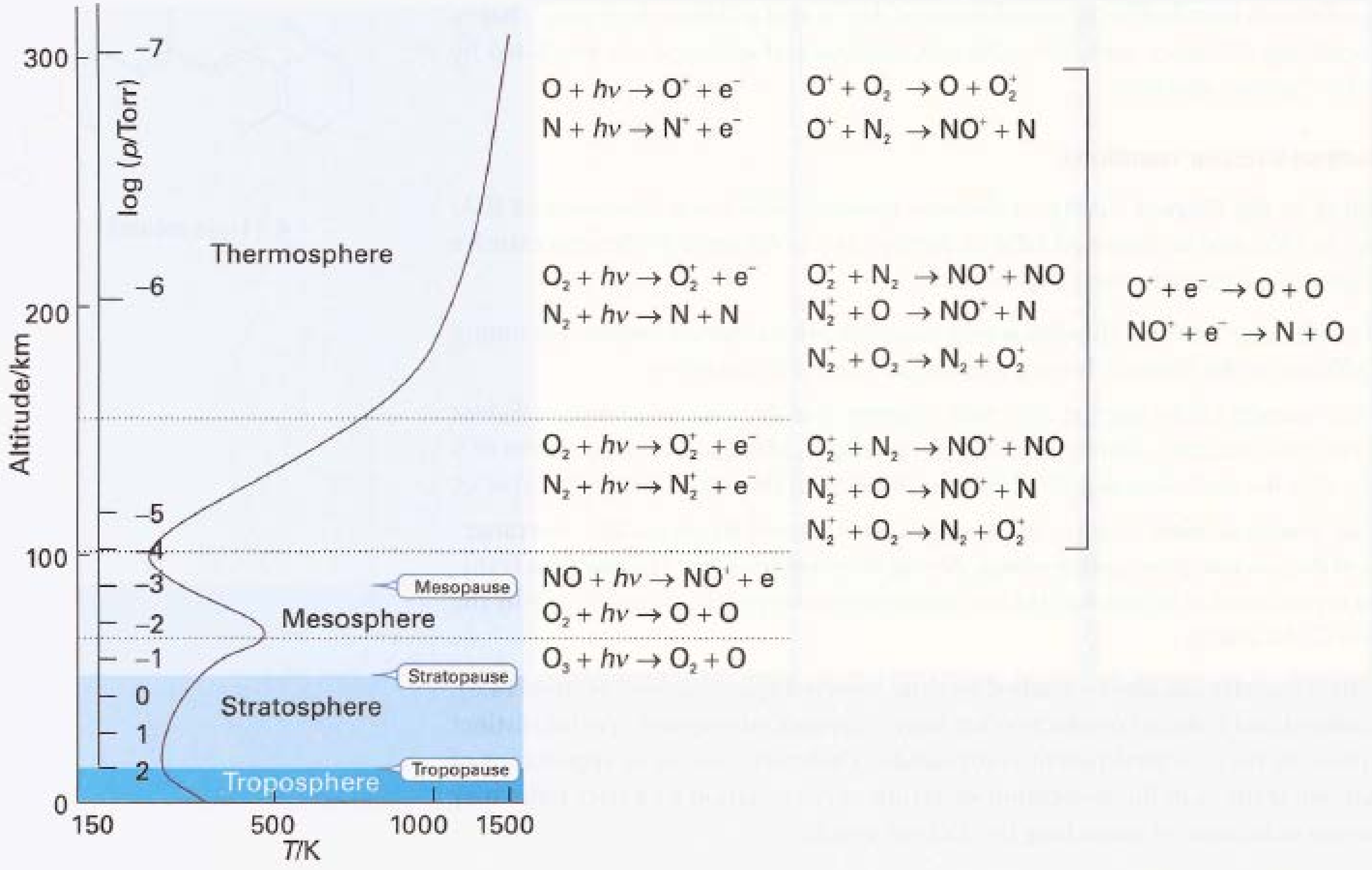
Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet–singlet	$S^* + S \rightarrow S + S^*$
Triple–triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet–singlet	$S^* + S^* \rightarrow S^{**} + S$
Triple–triplet	$T^* + T^* \rightarrow S^* + S$

† S denotes a singlet state, T a triplet state, and M is a third body.

Table 23.1 Examples of photochemical processes

Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \xrightarrow{134\text{ nm}} NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$[Ru(bpy)_3^{2+}]^* + Fe^{3+} \xrightarrow{452\text{ nm}} Ru(bpy)_3^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow B + C$	$O_3^* \xrightarrow{1180\text{ nm}} O_2 + O$
	$A^* + B{-}C \rightarrow A + B + C$	$Hg^* + CH_4 \xrightarrow{254\text{ nm}} Hg + CH_3 + H$
Addition	$2\,A^* \rightarrow B$	
	$A^* + B \rightarrow AB$	
Abstraction	$A^* + B{-}C \rightarrow A{-}B + C$	$Hg^* + H_2 \xrightarrow{254\text{ nm}} HgH + H$
Isomerization or rearrangement	$A^* \rightarrow A'$	

In gas phase



$O + h\nu \rightarrow O^+ + e^-$ $\quad$ $O^+ + O_2 \rightarrow O + O_2^+$

$N + h\nu \rightarrow N^+ + e^-$ $\quad$ $O^+ + N_2 \rightarrow NO^+ + N$

$O_2 + h\nu \rightarrow O_2^+ + e^-$ $\quad$ $O_2^+ + N_2 \rightarrow NO^+ + NO$

$N_2 + h\nu \rightarrow N + N$ $\quad$ $N_2^+ + O \rightarrow NO^+ + N$

$N_2^+ + O_2 \rightarrow N_2 + O_2^+$

$O_2 + h\nu \rightarrow O_2^+ + e^-$ $\quad$ $O_2^+ + N_2 \rightarrow NO^+ + NO$

$N_2 + h\nu \rightarrow N_2^+ + e^-$ $\quad$ $N_2^+ + O \rightarrow NO^+ + N$

$N_2^+ + O_2 \rightarrow N_2 + O_2^+$

$O^+ + e^- \rightarrow O + O$

$NO^+ + e^- \rightarrow N + O$

$NO + h\nu \rightarrow NO^+ + e^-$

$O_2 + h\nu \rightarrow O + O$

$O_3 + h\nu \rightarrow O_2 + O$

Fig. 23.17 The temperature profile through the atmosphere and some of the reactions that occur in each region.

Photochemistry

- Electron transitions by UV-vis light
  - σ orbitals (electrons in covalent bonds) $\rightarrow \sigma^*$
  - *n* orbitals (non-bonded electrons) $\rightarrow \pi^*$
  - π orbitals (C=C, C=O) $\rightarrow \pi^*$ (anti-bonding)

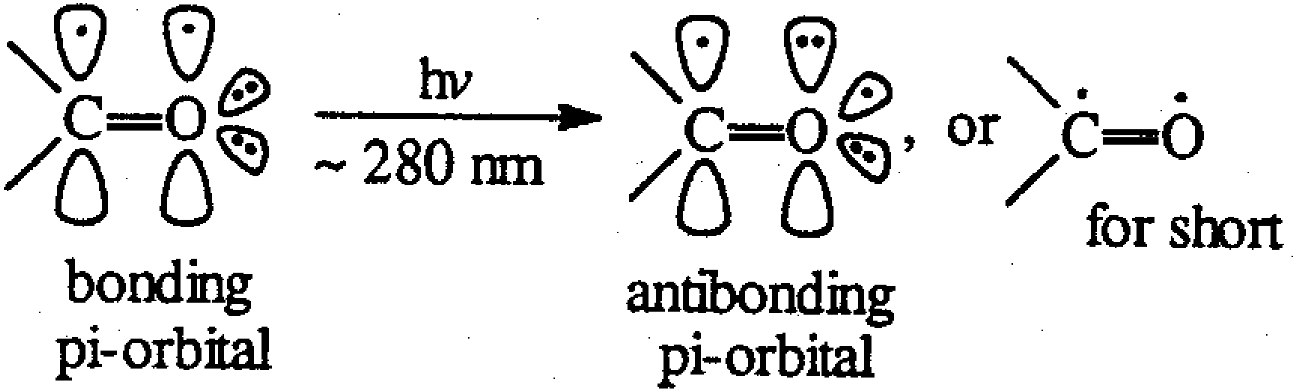
Photochemistry

- Electron transitions by UV-vis light
  - σ orbitals (electrons in covalent bonds) → σ^*
  - *n* orbitals (non-bonded electrons) → π^*
  - π orbitals (C=C, C=O) → π^* (anti-bonding)

- Chromophores
  - functional group that absorbs light
    - C, N, O ($n \rightarrow \pi^*$)
    - double bonds ($\pi \rightarrow \pi^*$)
  - characteristic absorption wavelength

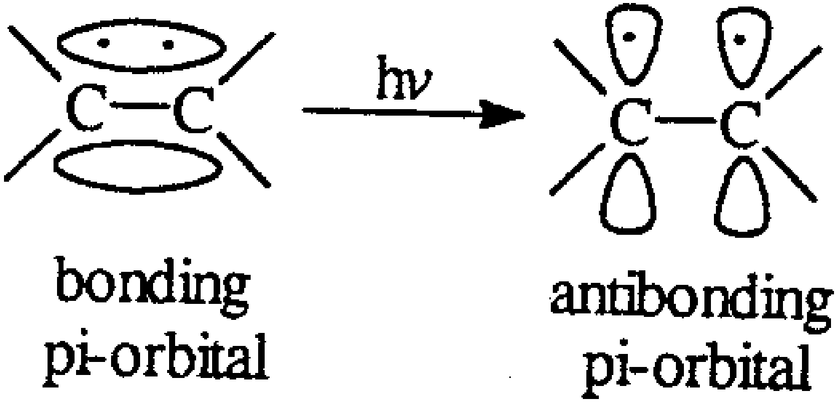
Photochemistry

- $n \rightarrow \pi^*$ transition
  - move one *n* electron to π^* orbital
  - two spin-paired, orbitally unpaired electrons
  - formation of di-radical
    - very electrophilic
    - acts as strong oxidant

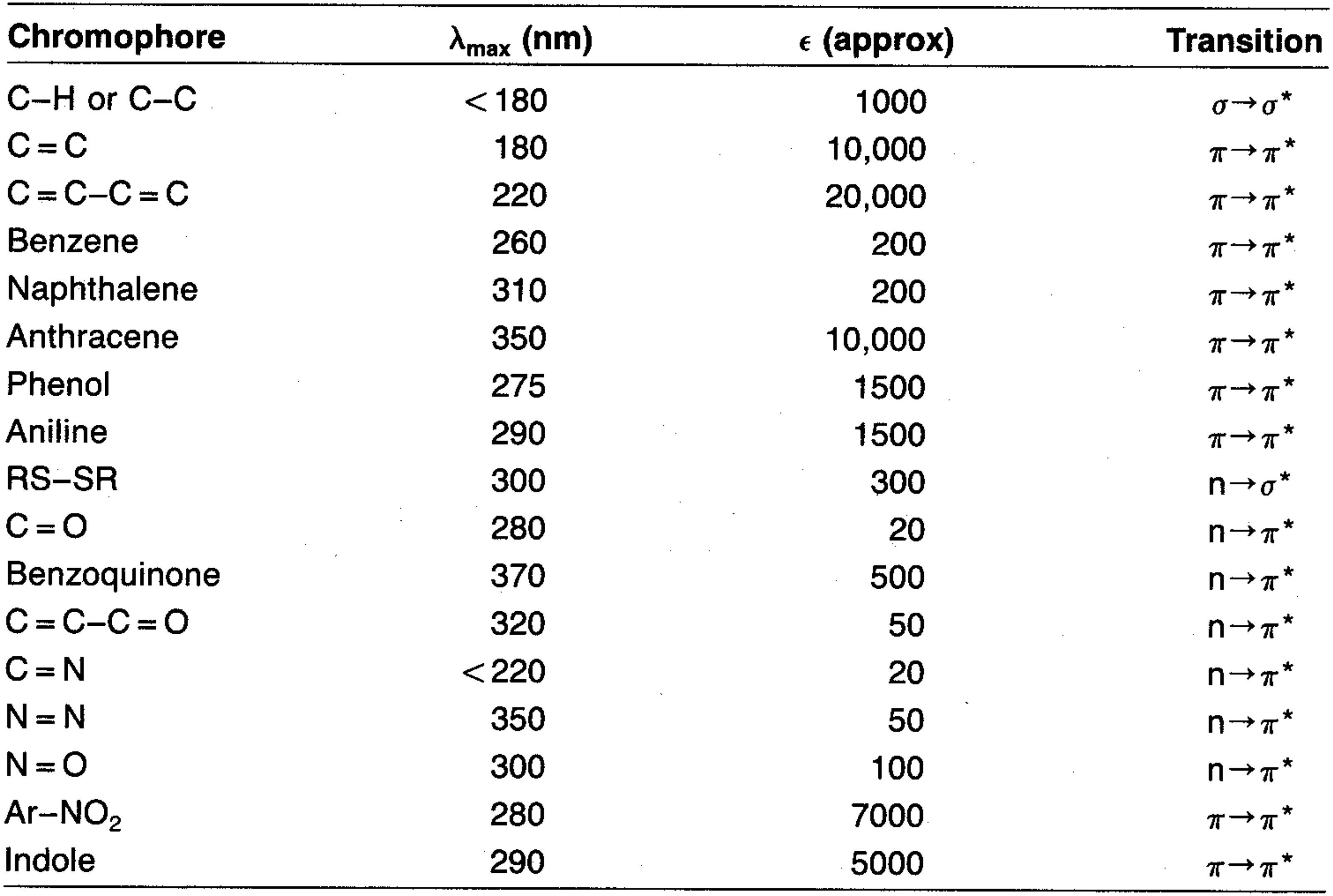


Photochemistry

- $\pi \rightarrow \pi^*$ transition
  - orbital unpairing of C=C bond electrons
  - formation of di-radical
    - very electrophilic
    - acts as strong oxidant
  - higher ε because electrons occupy same space



Photochemistry



Chromophore	λ_{max} (nm)	ϵ (approx)	Transition
C–H or C–C	<180	1000	$\sigma \rightarrow \sigma^*$
$C=C$	180	10,000	$\pi \rightarrow \pi^*$
$C=C-C=C$	220	20,000	$\pi \rightarrow \pi^*$
Benzene	260	200	$\pi \rightarrow \pi^*$
Naphthalene	310	200	$\pi \rightarrow \pi^*$
Anthracene	350	10,000	$\pi \rightarrow \pi^*$
Phenol	275	1500	$\pi \rightarrow \pi^*$
Aniline	290	1500	$\pi \rightarrow \pi^*$
RS–SR	300	300	$n \rightarrow \sigma^*$
$C=O$	280	20	$n \rightarrow \pi^*$
Benzoquinone	370	500	$n \rightarrow \pi^*$
$C=C-C=O$	320	50	$n \rightarrow \pi^*$
$C=N$	<220	20	$n \rightarrow \pi^*$
$N=N$	350	50	$n \rightarrow \pi^*$
$N=O$	300	100	$n \rightarrow \pi^*$
$Ar-NO_2$	280	7000	$\pi \rightarrow \pi^*$
Indole	290	5000	$\pi \rightarrow \pi^*$

Source: Scott (1964) and Turro (1978).

Photochemistry

- Direct photolysis
  - compound is transformed by light absorbed by the compound

- Indirect photolysis
  - compound is transformed by reaction with an compound excited by the absorption of light by other compound. Transformation of a compound due to its interaction with a reactant generated by the influence of UV light (photosensitizer or reactive oxygen species)

Direct Photolysis

- compound that absorbs light is the one that reacts
- need to know three things:
  - light spectrum
    - depends on time of day, season, latitude, cloud cover, etc.
  - light absorption spectrum
    - depends on chromophores in compound
  - quantum yield ϕ
    - ratio of the compound that undergoes reaction to the compound that is converted to an excited state
    - reaction is just one pathway of return from excited state
    - function of wavelength $\phi(\lambda)$