Chemistry 471/671

Atmospheric Chemistry I:
The Troposphere

Air Pollution

Urban air pollution is the oldest recorded concern of society with regards to the environment

The Mishnah Laws required tanneries to be located at least 50 cubits (~25 m) east of town (Israel, first century A.D.)

Moses Maimonides: “Comparing the air of cities to the air of deserts and arid lands is like comparing waters that are befouled and turbid to waters that are clean and pure... the air becomes stagnant, turbid, thick, misty, and foggy... Therefore you find many men in whom you can notice defects in the actions of the psyche with the spoilage of the air, namely, that they develop dullness of understanding, failure of intelligence and defect of memory.” (Cairo, late 12th century)

Urban Air Pollution – “London” Smog

In the 17th century, John Evelyn published a treatise on air pollution in London, caused by the widespread use of high-sulfur coal:

“It is this horrid Smoake which obscures our Church and makes our Palaces look old... which, with its black and tenacious quality, spots and contaminates whatever is exposed to it.”

“... near half the children who are born and bred in London die under two years of age... the constant and unremitting Poison is communicated by the foul Air, which, as the Town still grows larger, has made regular and steady advances in its fatal influence.”

Urban Air Pollution

What is smog?

Where does it come from?

What can we do about it?

What constitutes “clean” air?

What do we put into the air that makes things go so wrong?

Composition of the Atmosphere

Compound	Formula	Percent by volume
Nitrogen	N_2	78%
Oxygen	O_2	21%
Water	H_2O	*0 to 4%**
Argon	Ar	0.93%
Carbon Dioxide	CO_2	*0.0360%**
Neon	Ne	0.0018%
Helium	He	0.0005%
Methane	CH_4	*0.00017%**
Hydrogen	H_2	0.00005%
Nitrous Oxide	N_2O	*0.00003%**
Ozone	O_3	*0.000004%**

Chemical Reactivity

What do we mean when we say that a molecule is "reactive"?

Generally, we mean that a molecule reacts quickly. What determines how quickly a reaction will take place?

You will hopefully recall...

For a simple reaction, $X + Y \rightarrow Z$

We can define a rate such that

$$\text{Rate} = k[X]^x[Y]^y$$

k = rate constant
[X] = concentration of reactant X
x = order of the reaction with respect to reactant X

Gas phase kinetics

$$\text{Rate} = k[X]^x[Y]^y$$

Concentration: What units do we normally consider?

Are these units good for ideal gases?

In the gas phase, we generally express concentrations in terms of partial pressures, or in molecules/cm^3.

Having picked a unit for concentration, what effect does altitude have on the concentration of a given reactant?

Gas phase kinetics

$$\text{Rate} = k[X]^x[Y]^y$$

Rate constant: What factors affect the value of the rate constant?

The Arrhenius equation:

$$k(T) = A\, e^{(-Ea/RT)}$$

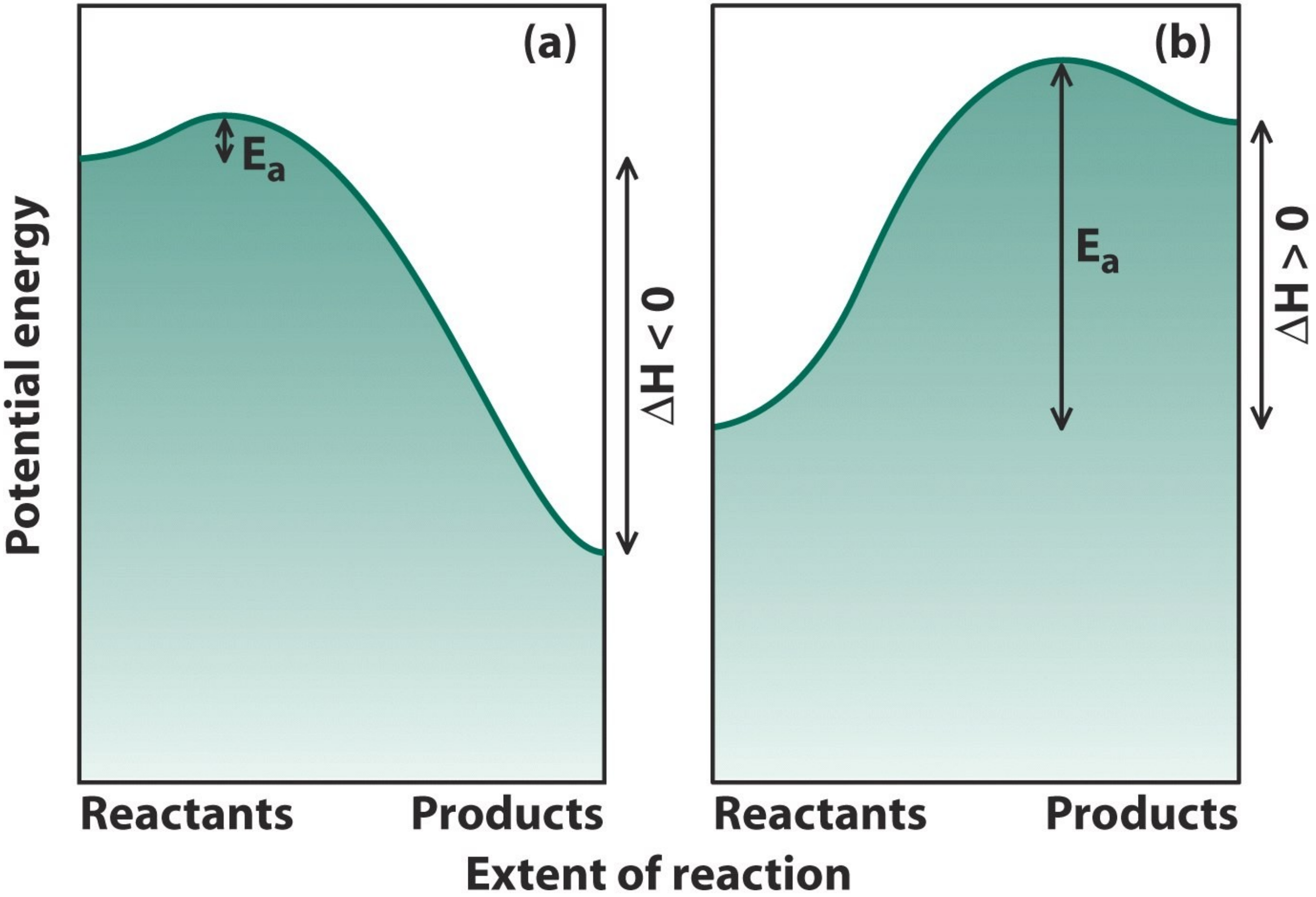
Temperature, activation energy, “the A-Factor”.

What happens to the rate constant as A increases?

as Ea increases?

as T increases?

Gas phase kinetics



Box 1-1
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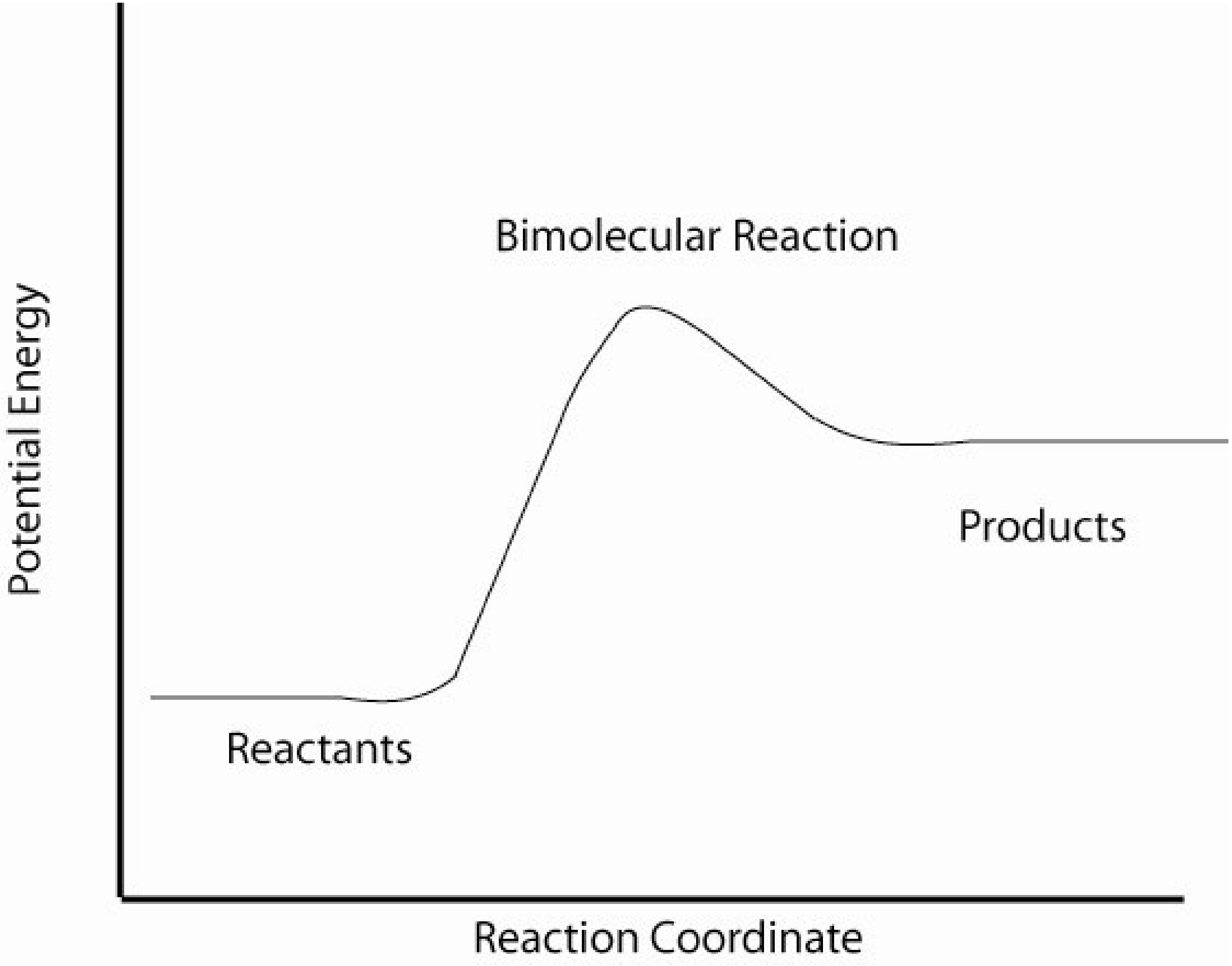
Gas Phase Kinetics: Order and Molecularity

In a simple, one-step reaction, the sum of the reaction orders with respect to each reagent is called the “molecularity” of the reaction.

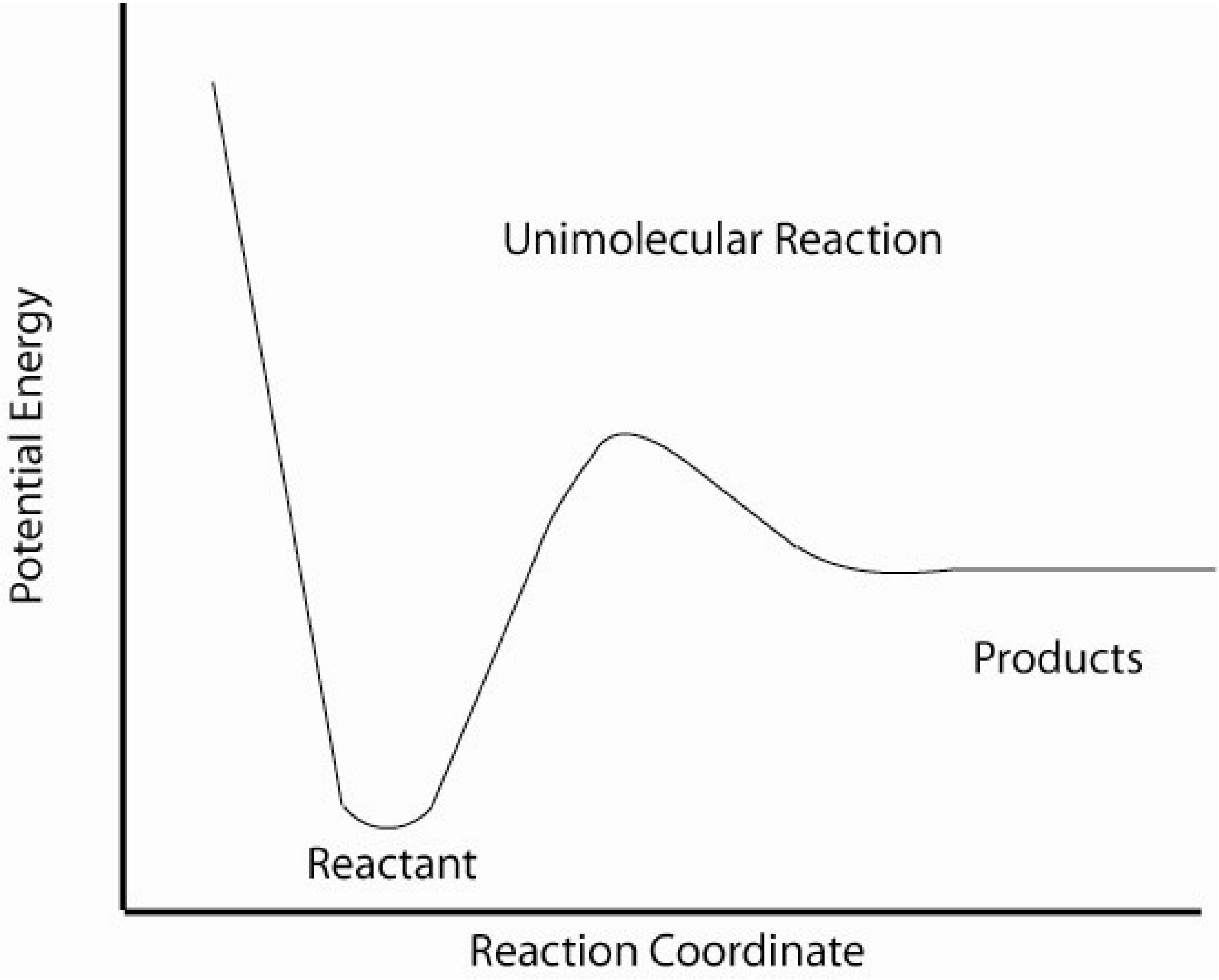
This number represents the total number of molecules which are involved in the process.

In elementary processes, we need only consider unimolecular, bimolecular and termolecular reactions.

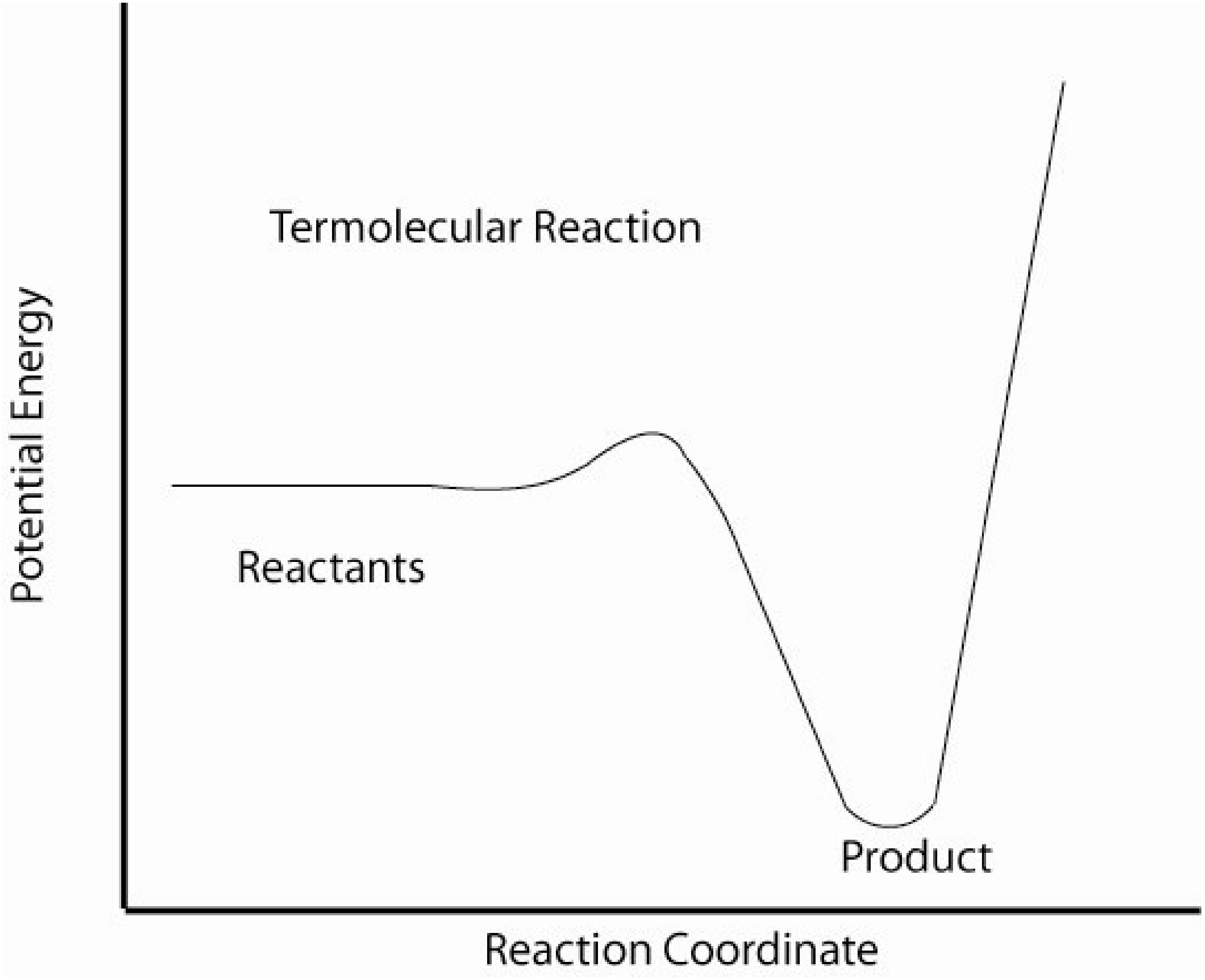
Gas Phase Kinetics: Bimolecular Reactions



Gas Phase Kinetics: Unimolecular Reactions



Gas Phase Kinetics: Termolecular Reactions



Gas phase kinetics

What **is** the "A-Factor"?

"Pre-exponential factor", "Arrhenius factor", "Frequency factor"

It's a measure of probability... Or, more precisely, of *entropy.*

It is dependent on several factors, including the geometry of the transition state

It reflects the likelihood that any given collision will produce a reaction

- Are the molecules aligned correctly?
- How "difficult" is it *entropically* to rearrange from reactant to transition state?

It is NOT necessarily temperature-independent!

Gas phase kinetics

$$X + Y \rightarrow Z$$

What has to happen for our simple reaction to proceed?

T 1) Two molecules have to collide

A 2) They have to collide in the correct orientation to react

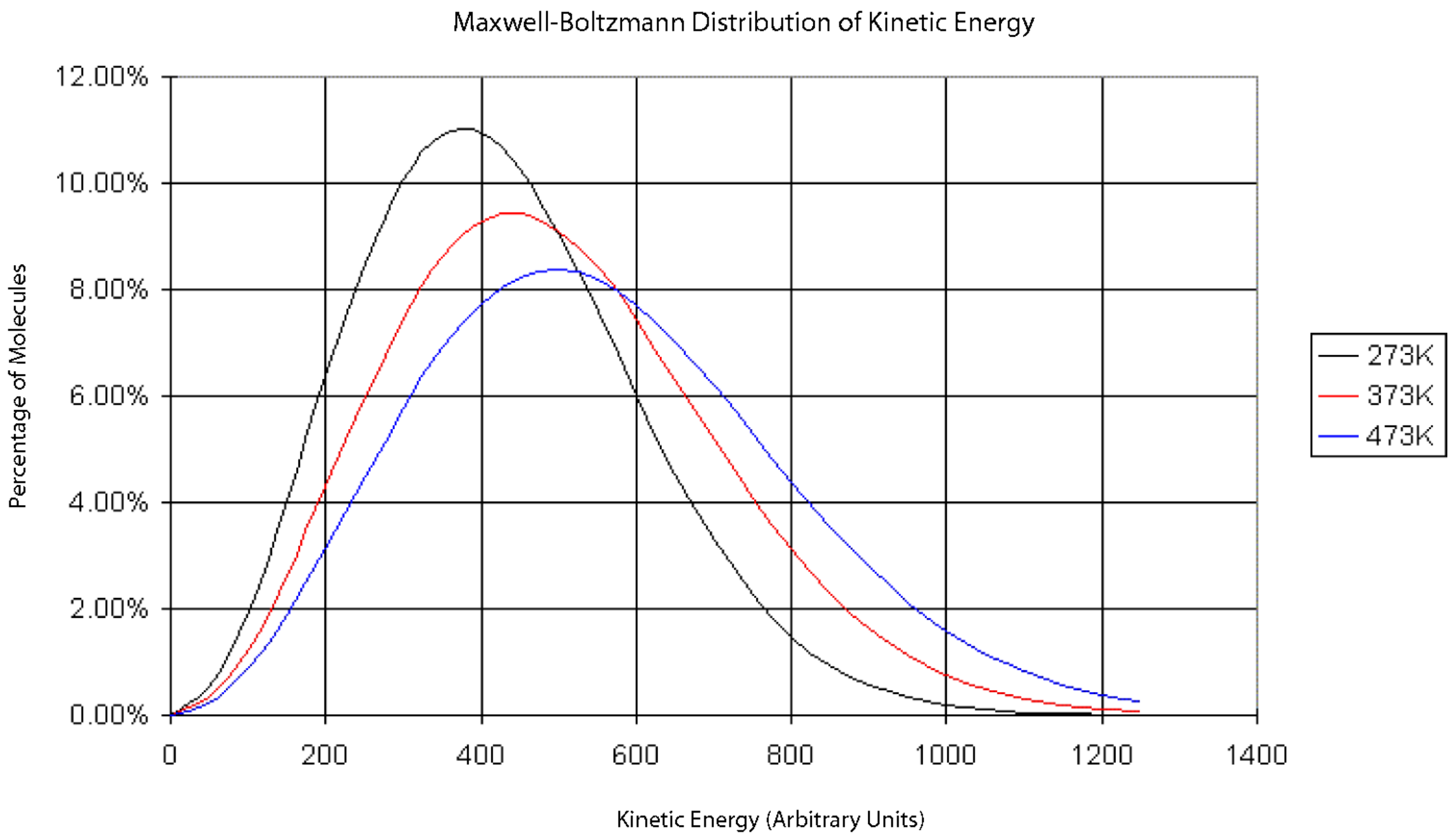
T, Ea 3) They have to collide with sufficient energy to make and break chemical bonds

How do these requirements correlate with the terms of the Arrhenius equation? (A, Ea, T)

Gas phase kinetics

Recall the Maxwell-Boltzmann Distribution of Kinetic Energy:

$$f\,(E) = N_E/N \propto e^{-E/RT}$$



Gas phase kinetics

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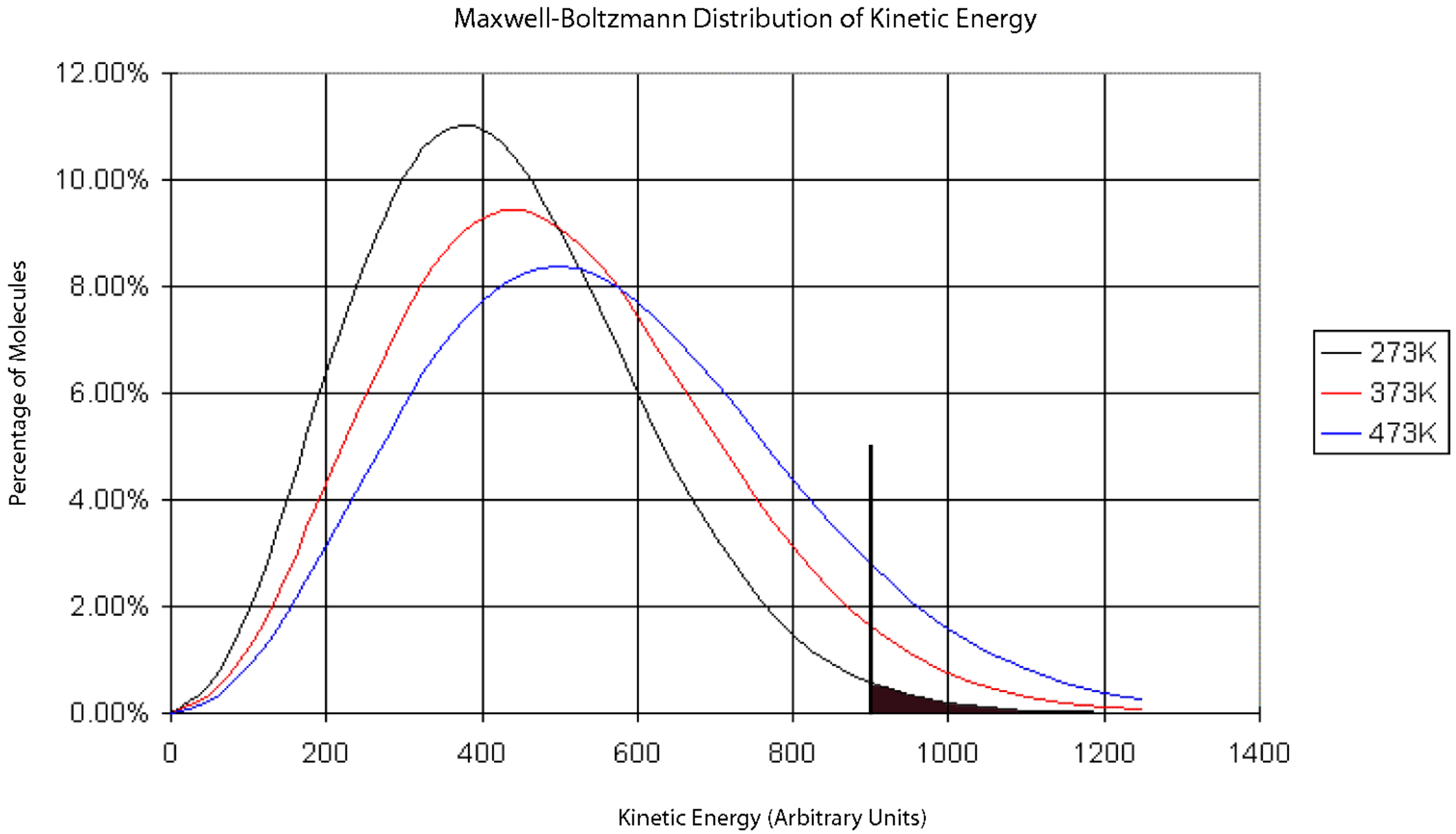

Gas phase kinetics

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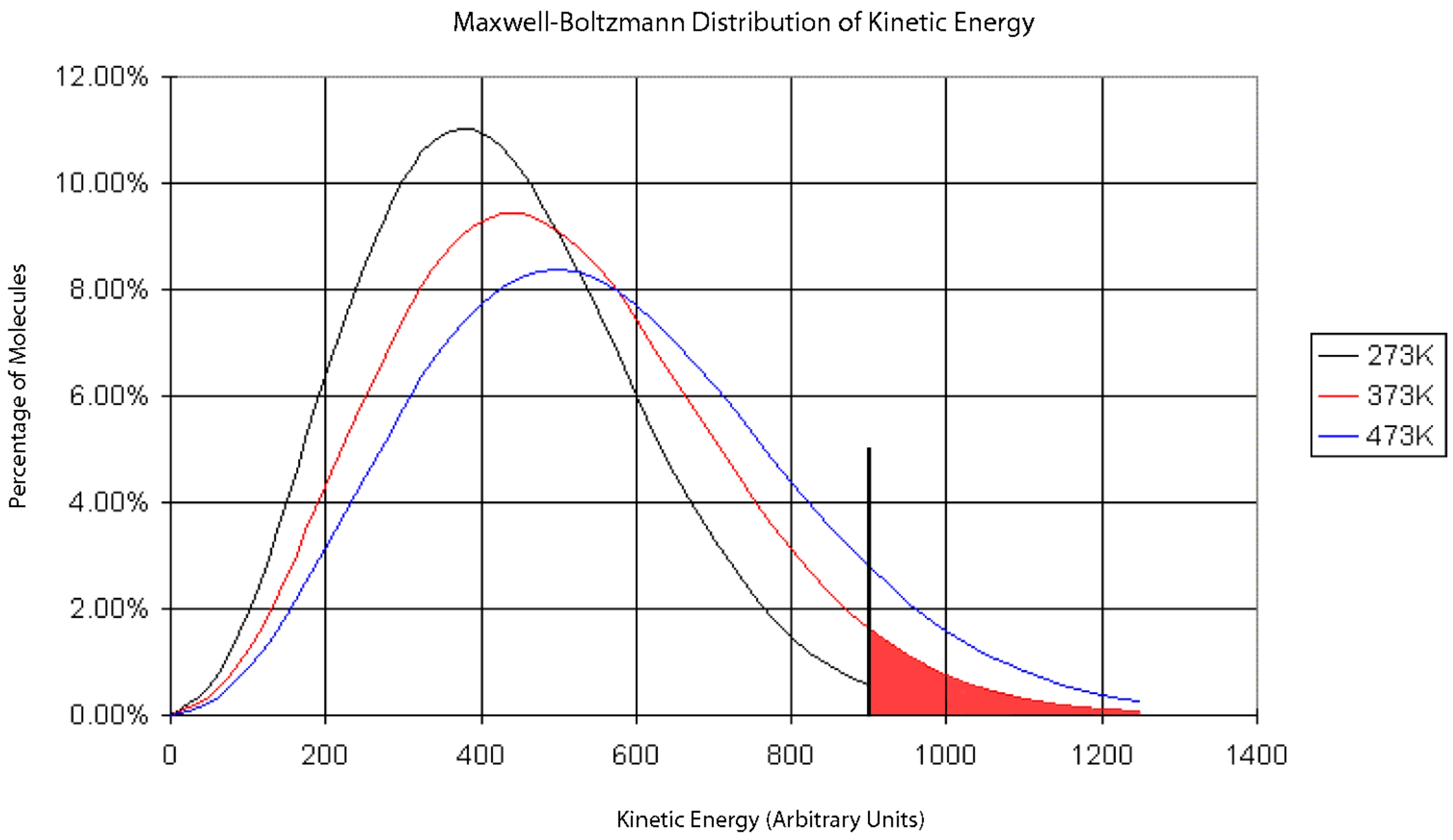

Gas phase kinetics

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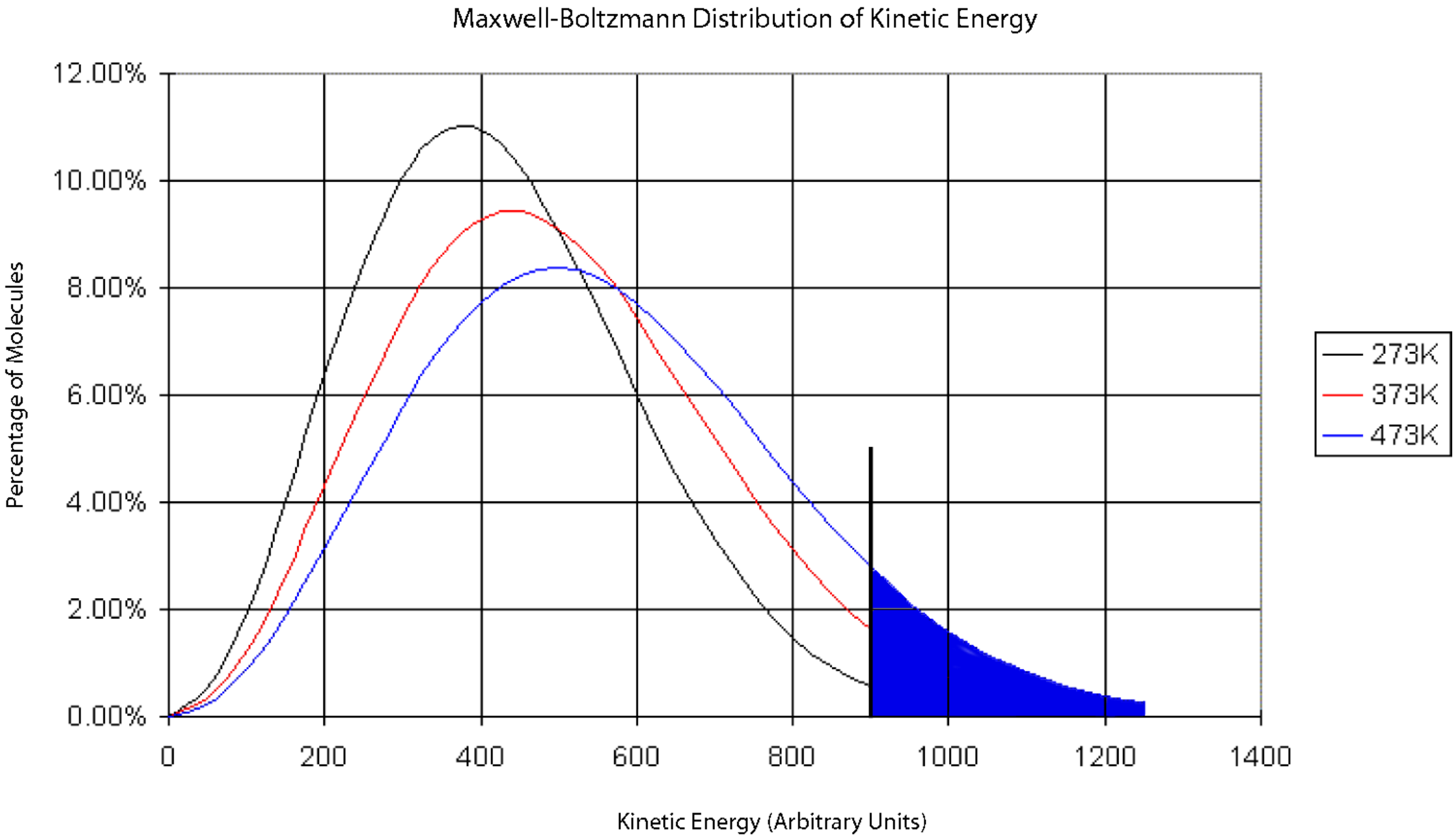


Gas phase kinetics

$$\text{Rate} = k[X]^x[Y]^y$$

What happens to the rate constant as A increases?

as Ea increases?

as T increases?

What effect does altitude have on the rate?

Gas phase kinetics

Rate = $k[X]^x[Y]^y$

So, as altitude increases, the concentration of both A and B decrease.

And, as altitude increases, the rate constant is likely to decrease.

When is this not the case?

Thus, the overall rate of **most** reactions is much higher at lower elevations.

This means that the chemistry of the atmosphere gets less complex as altitude increases: fewer and fewer reactions matter once temperature and pressure have dropped off significantly.

Which reactions DO matter?

Radicals.

Gas phase kinetics

Which radicals?

And where do they come from?

O_3 (ozone) – from the Chapman mechanism

$O(^1D)$ (atomic, excited oxygen) – Chapman mechanism

OH (hydroxyl) – from the photolysis of water vapor

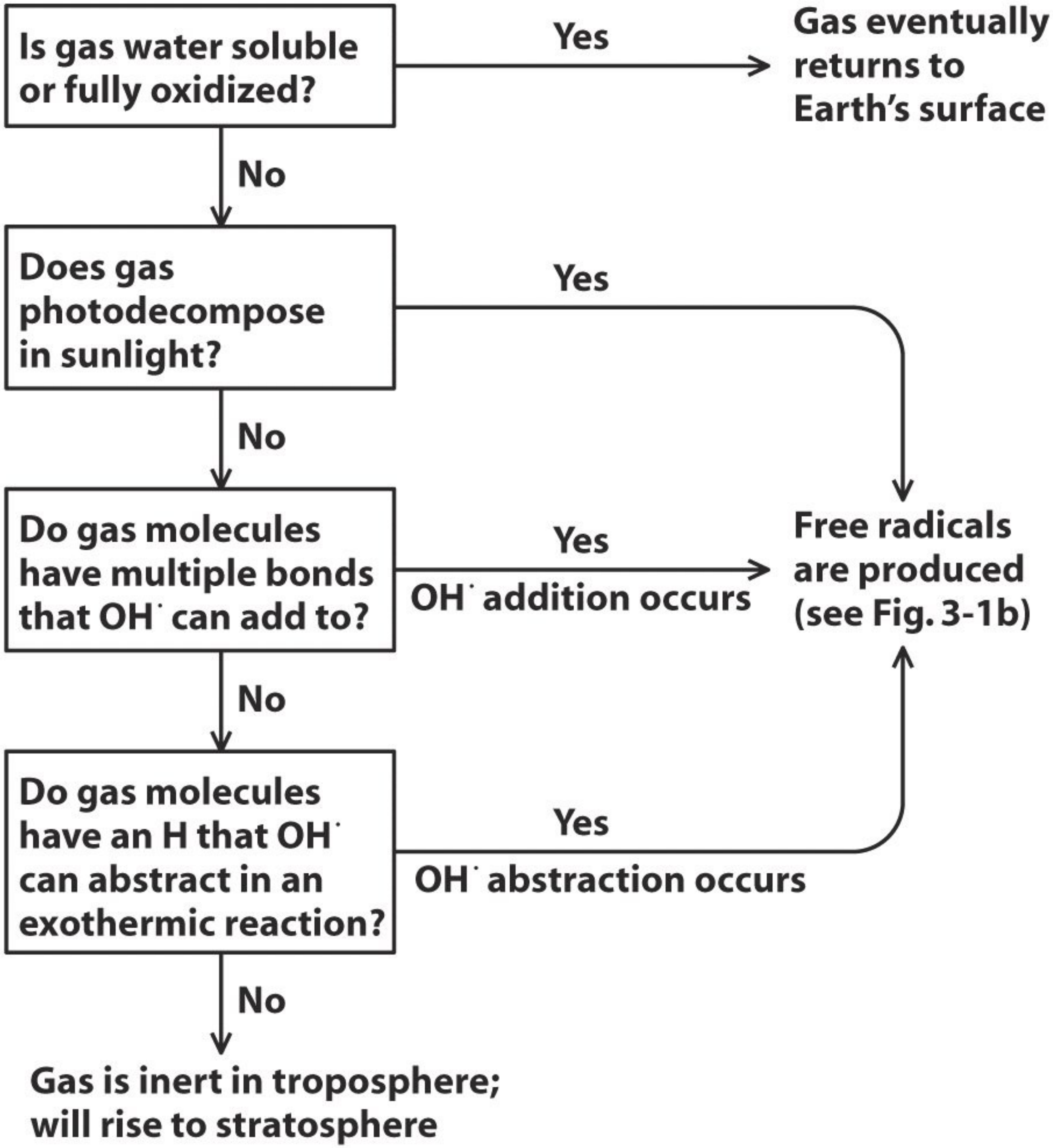
HO_2 (hydroperoxyl) – from photolysis of water vapor and reaction of H with diatomic oxygen

NO (nitric oxide) – from the reaction of N_2O with $O(^1D)$

NO_2 (nitrogen dioxide) – from the reaction of NO with O_2, O_3 and $O(^1D)$

Gas phase kinetics

What happens to any arbitrarily selected molecule that makes its way into the atmosphere?



Is gas water soluble or fully oxidized?

Yes

Gas eventually returns to Earth's surface

No

Does gas photodecompose in sunlight?

Yes

No

Do gas molecules have multiple bonds that $OH^{\cdot}$ can add to?

Yes

$OH^{\cdot}$ addition occurs

Free radicals are produced (see Fig. 3-1b)

No

Do gas molecules have an H that $OH^{\cdot}$ can abstract in an exothermic reaction?

Yes

$OH^{\cdot}$ abstraction occurs

No

Gas is inert in troposphere; will rise to stratosphere

Figure 3-1a
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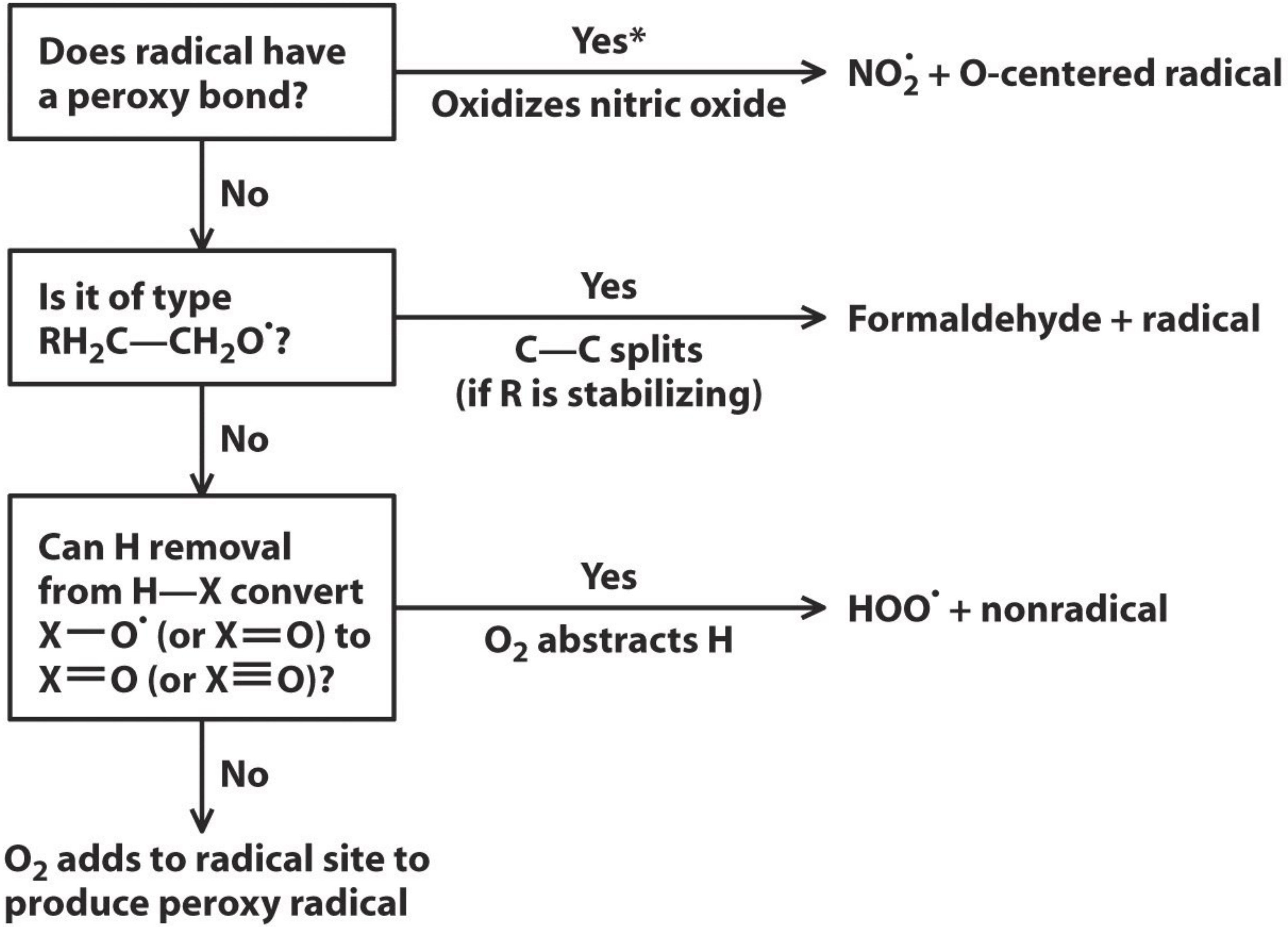

Does radical have a peroxy bond?

Yes* — Oxidizes nitric oxide → $NO_2^{\bullet}$ + O-centered radical

No ↓

Is it of type $RH_2C—CH_2O^{\bullet}$?

Yes — C—C splits (if R is stabilizing) → Formaldehyde + radical

No ↓

Can H removal from H—X convert $X—O^{\bullet}$ (or $X{=}O$) to $X{=}O$ (or $X{\equiv}O$)?

Yes — O_2 abstracts H → $HOO^{\bullet}$ + nonradical

No ↓

O_2 adds to radical site to produce peroxy radical

*Under conditions with significant nitric oxide present and before radical + radical reactions become important.

Figure 3-1b

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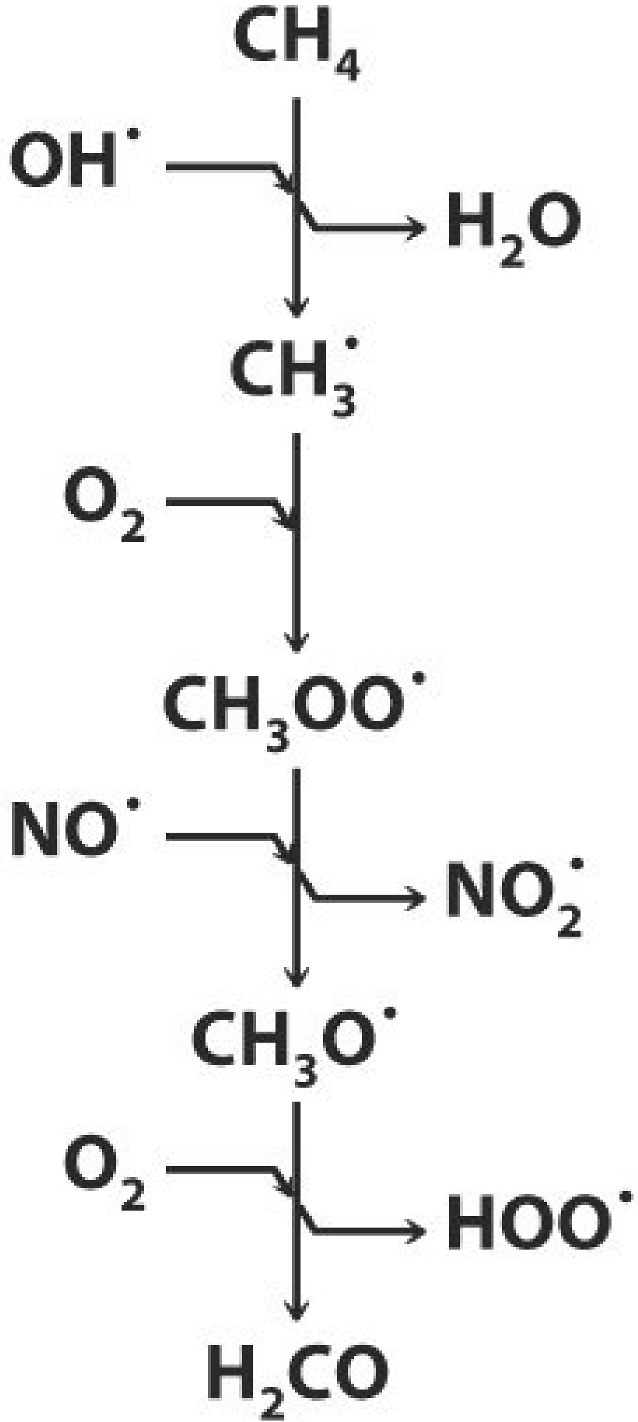
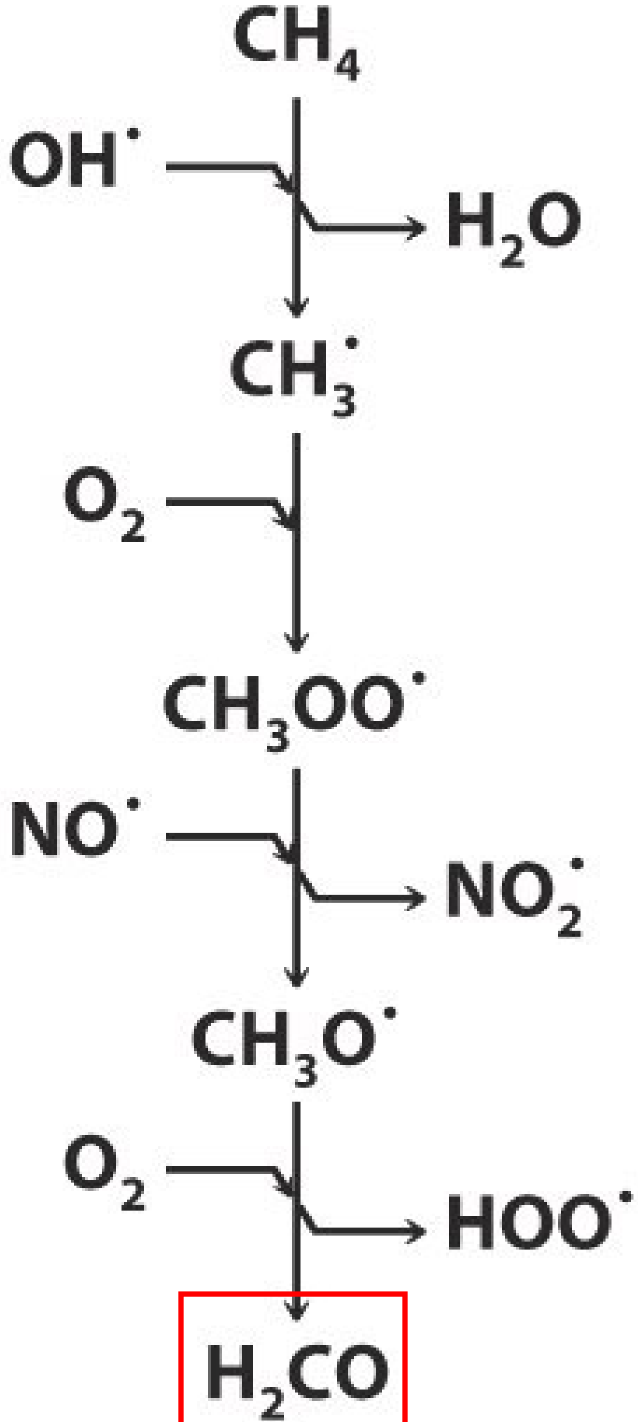


The Oxidation of Methane

Does it photodecompose in sunlight?

Does it have double bonds that can add OH?

Does it have H atoms that can be abstracted by OH?



The Oxidation of Methane

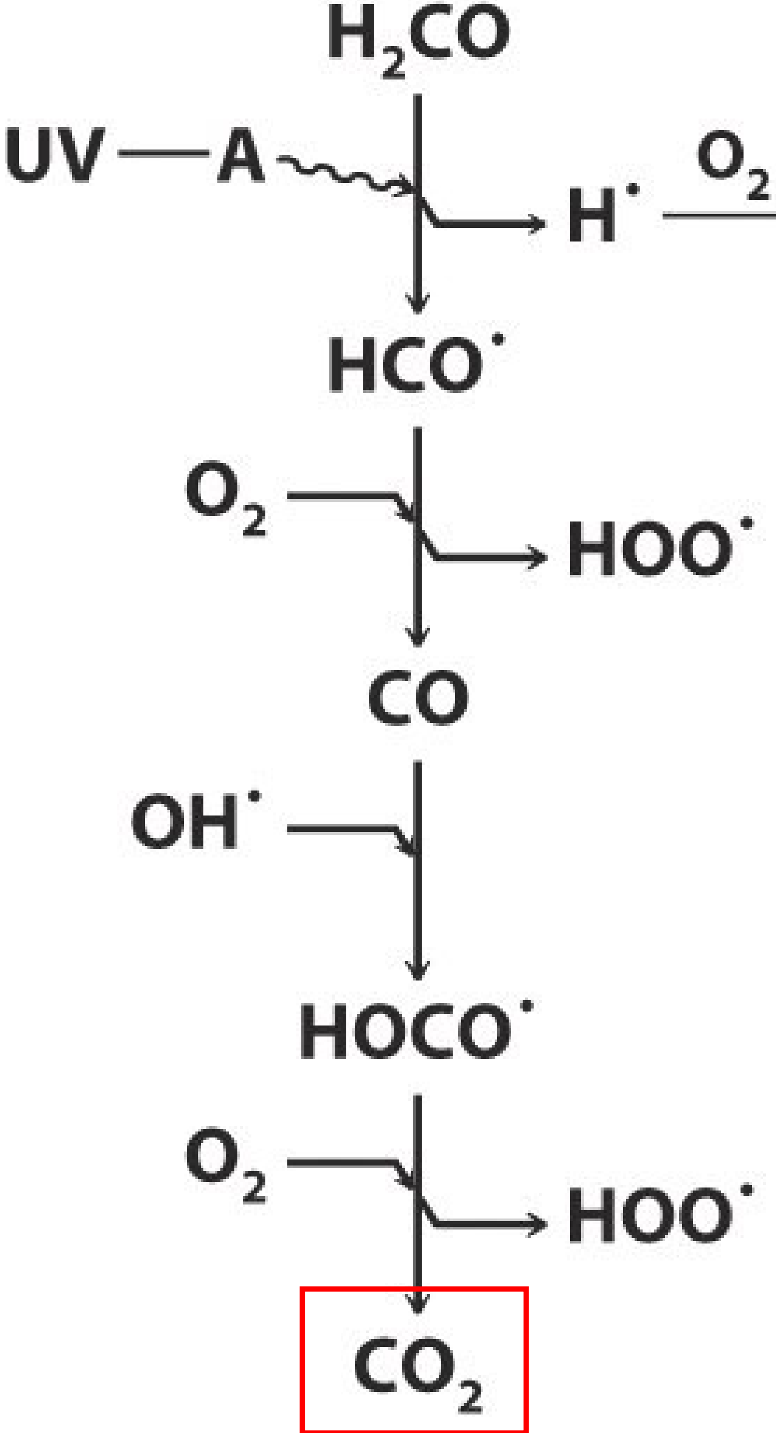
Does it have a peroxy bond?

Can I make formaldehyde from it?

Can I abstract an H to make a multiple bond to oxygen?

If no to all of the above, add O_2

The Oxidation of Methane



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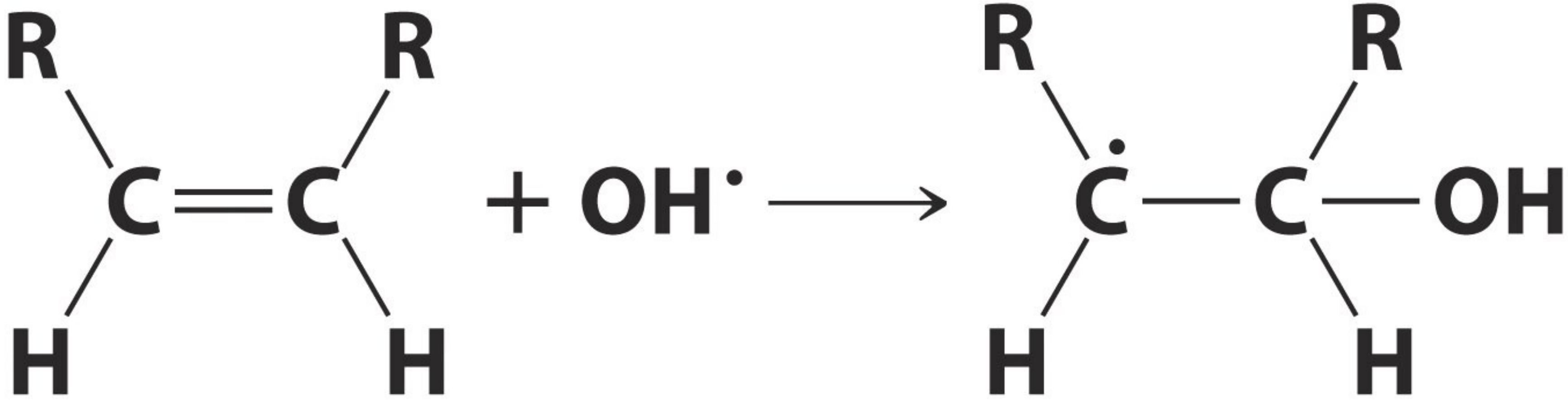
$$HO_2 + NO \rightarrow OH + NO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

The Oxidation of Reactive Hydrocarbons - Alkenes



Unnumbered Figure, pg 149-2
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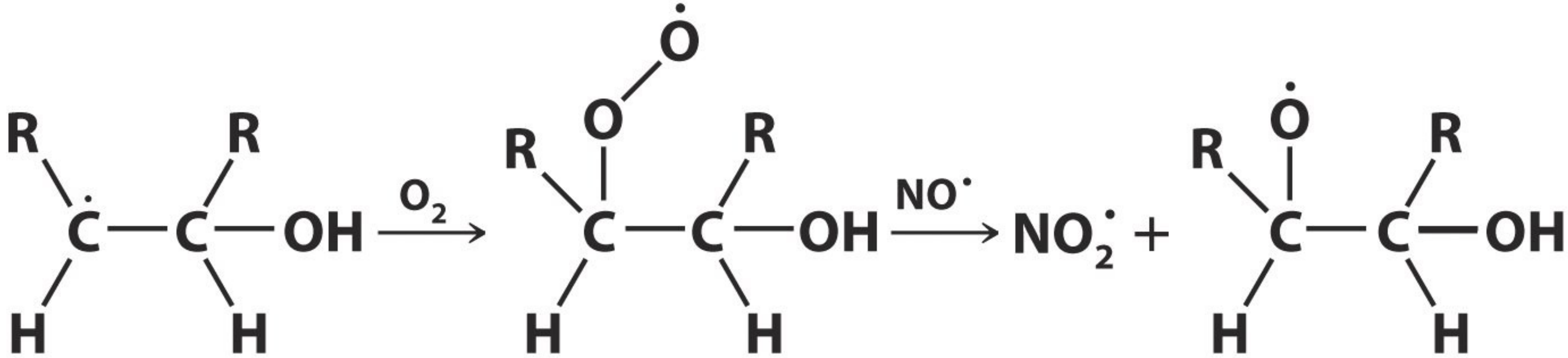
The Oxidation of Reactive Hydrocarbons - Alkenes



Unnumbered Figure, pg 150-1
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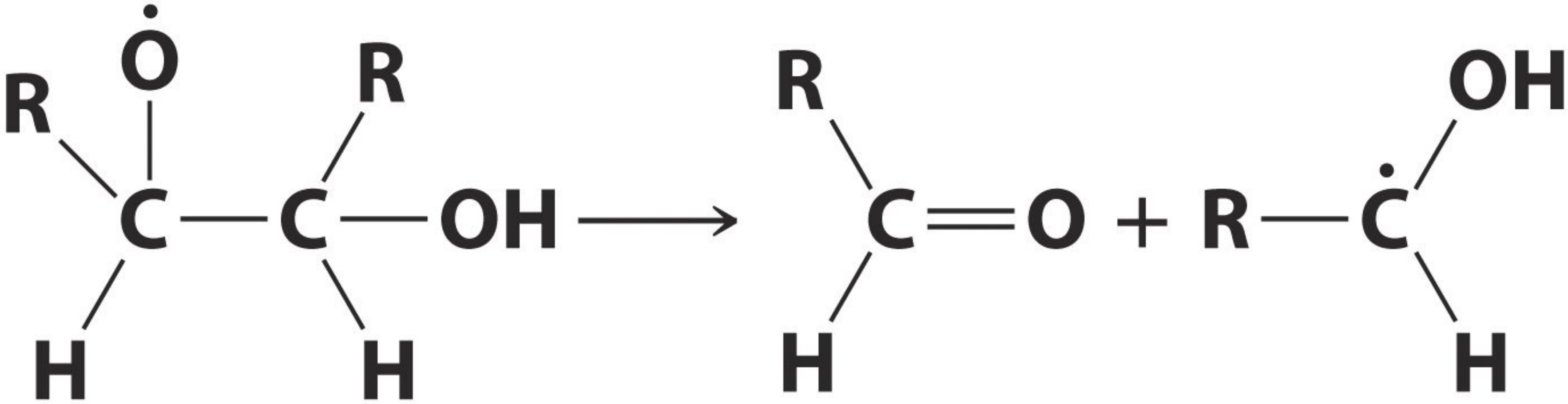
Does it have a peroxy bond?

Can I make formaldehyde from it?

Can I abstract an H to make a multiple bond to oxygen?

If no to all of the above, add O_2

The Oxidation of Reactive Hydrocarbons - Alkenes



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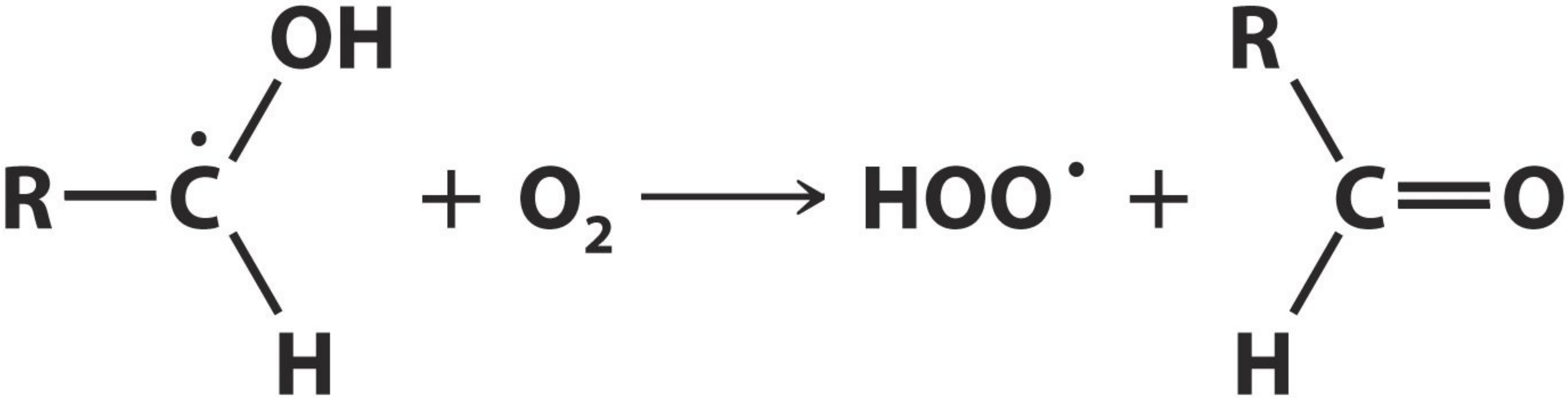
An aldehyde

The Oxidation of Reactive Hydrocarbons - Alkenes



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An aldehyde

Does it have a peroxy bond?

Can I make formaldehyde from it?

Can I abstract an H to make a multiple bond to oxygen?

If no to all of the above, add O_2

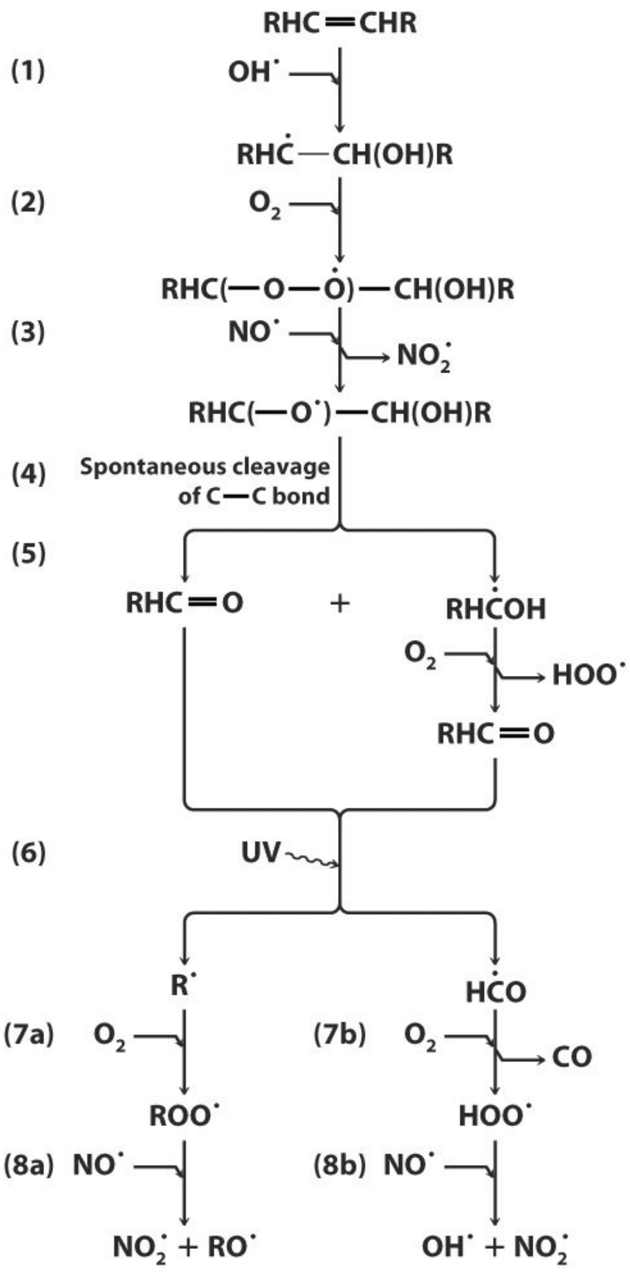

Figure 3-4
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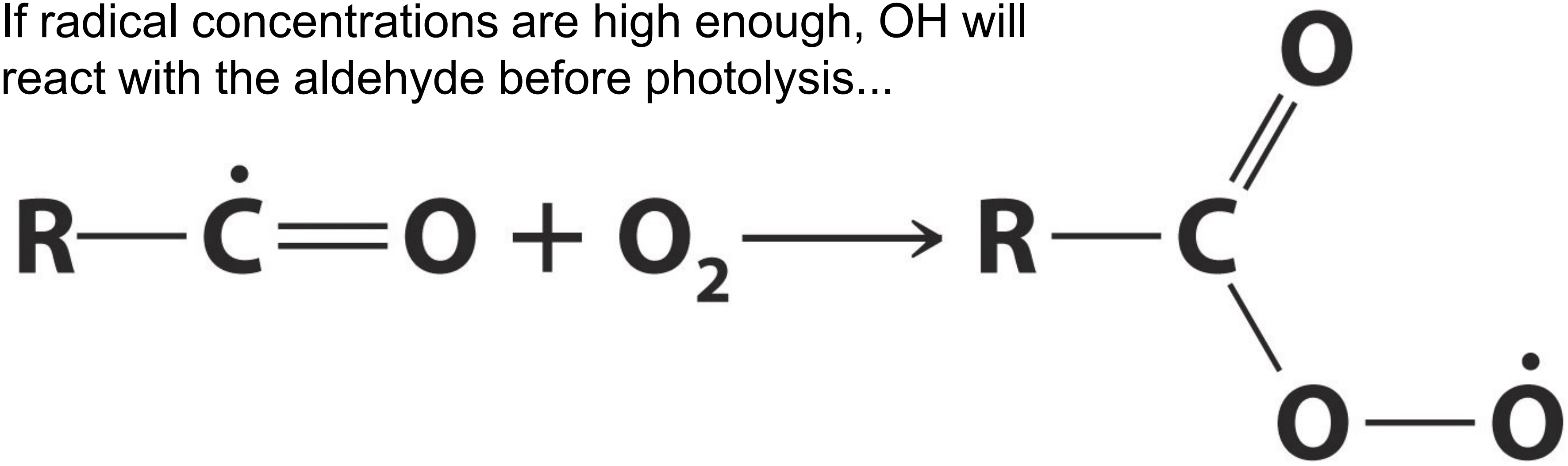
The Oxidation of Reactive Hydrocarbons - Alkenes

If radical concentrations are high enough, OH will react with the aldehyde before photolysis...



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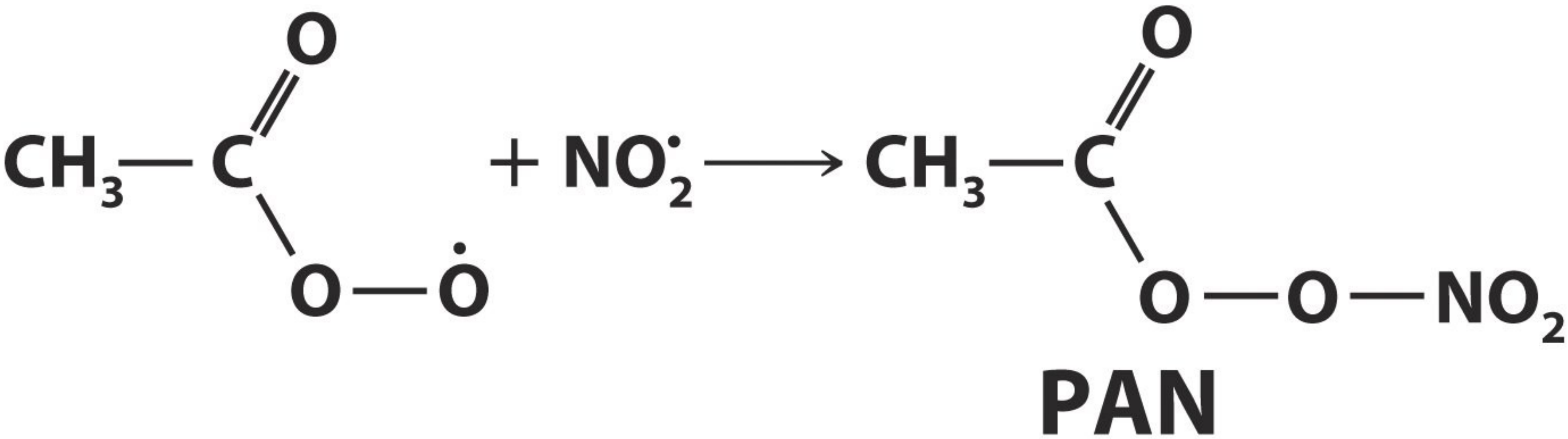
peroxyacetyl

In the afternoon, when [NO] is low and [NO_2] is high...



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Chain Termination:
the fate of the free radicals

- $OH + NO_2 \rightarrow HONO_2$
  photolabile, water soluble
- PAN formation
  photolabile, thermally short-lived
- $OH + NO \rightarrow HONO$
  photolabile
- $2\ OH \rightarrow H_2O_2$
  water soluble
- $2\ HO_2 \rightarrow H_2O_2 + O_2$
  water soluble
- $NO_2 + O_3 \rightarrow NO_3 + O_2$
  "dark oxidation"

Fate of VOCs

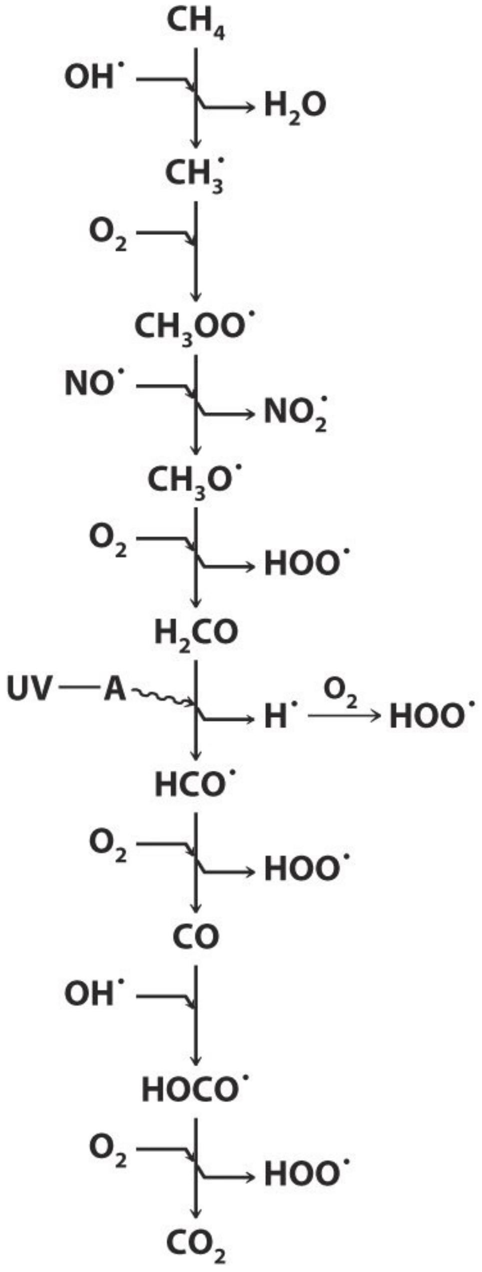

Figure 3-2
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This picture presents a common image: a single unbranched chain of compounds in the oxidation cycle

Statistics

- The list of steps taken is the most likely, and *most* molecules will indeed oxidize this way
- But not all – some molecules will have sufficient energy to clear higher activation barriers
- In addition, we're already making some assumptions about relative concentrations

Fate of VOCs

In reality, most oxidation schemes produce an array of products

Dependent on a variety of factors

- Temperature
- Pressure
- Concentrations
  - – and thus location

The distribution of products among the available channels is described by a “Branching Ratio”, β

Most easily defined as the ratio of product concentrations

But this also implies a fixed ratio of rate constants

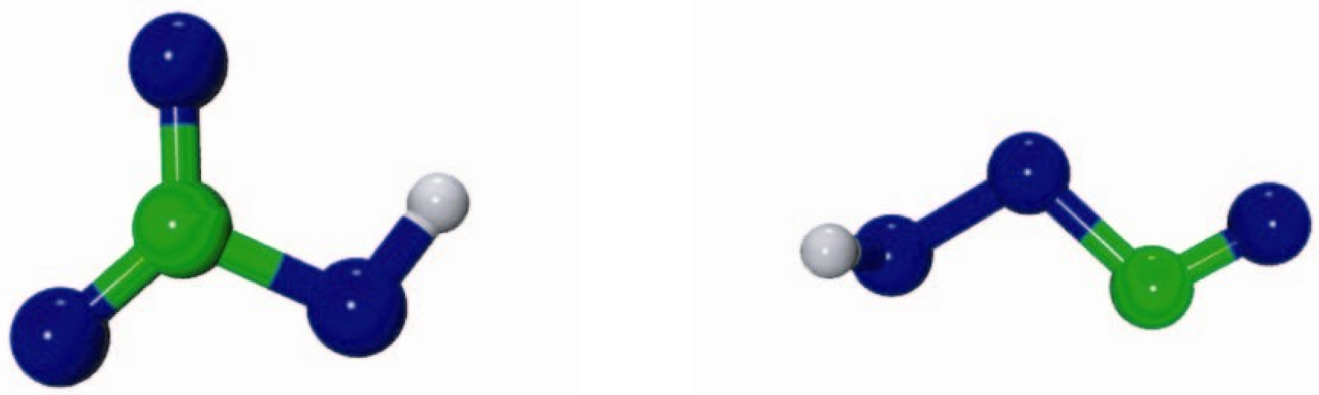
$\beta_i = k_i/\Sigma k_i$

Branching Ratio: A Simple Example

Take the reaction of OH + NO_2

$OH + NO_2 \rightarrow HONO_2$

But is that the only possible product?



Branching Ratio
A Complex Examp

The Atmospheric Oxidation of Acrolein