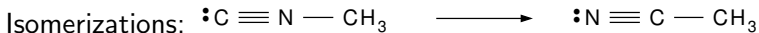


Foundations of Chemical Kinetics Lecture 11:  
Unimolecular reactions in the gas phase:  
The Lindemann mechanism

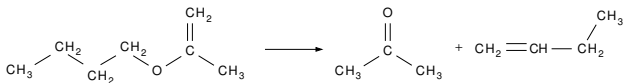
Marc R. Roussel

October 19, 2021

# Examples of unimolecular reactions in the gas phase



Decompositions:



What makes these reactions happen?

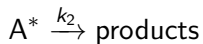
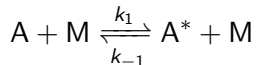
## General behavior of unimolecular reactions

- These reactions are generally carried out with a “bath gas” (M) for which  $[M] \gg [A]$  ( $[A]$  = reactant).
- At low pressures, the rate law has partial orders with respect to A and M of 1 each, so an overall order of 2.
- At high pressures, first-order kinetics in  $[A]$  is observed.

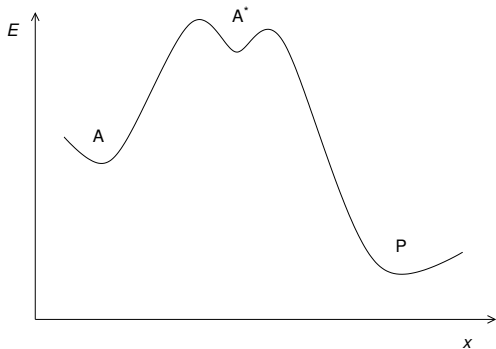
These observations are both

- 1 a clue as to the mechanism, and
- 2 a puzzle to be solved.

# The Lindemann mechanism

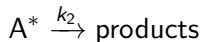
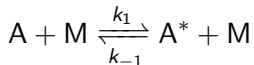


Implied potential energy profile:



# The Lindemann mechanism

Rate equations



Rate equations:

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

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

- There is no way to solve these equations exactly.

# The Lindemann mechanism

## Steady-state approximation

- There is a low barrier for reaction of  $A^*$ , so we expect  $k_{-1} \gg k_1$  and  $k_2 \gg k_1[M]$ .
- This is a perfect situation for the steady-state approximation.

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] \approx 0$$
$$\therefore [A^*] \approx \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$
$$\therefore v = k_2[A^*] \approx \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

# The Lindemann mechanism

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

- Low-pressure limit:
- High-pressure limit:

# The Lindemann mechanism

Interpretation of the high-pressure limit

- Suppose that the reaction  $A + M \xrightleftharpoons[k_{-1}]{k_1} A^* + M$  was the only one occurring.
- When this reaction reached equilibrium, we would have

$$k_1[A][M] = k_{-1}[A^*][M]$$

$$\therefore \frac{[A^*]}{[A]} = \frac{k_1}{k_{-1}} = K_1$$

where  $K_1$  is the equilibrium constant for this reaction.

- The high-pressure limit of the Lindemann rate equation is therefore

$$v \approx K_1 k_2 [A]$$



# The Lindemann mechanism

A slight rewrite

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

with  $k_L = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$ .

Define  $k_\infty = k_1 k_2 / k_{-1}$  (high-pressure limit of  $k_L$ )

Then,  $k_L = \frac{k_\infty [M]}{[M] + k_\infty / k_1}$ .

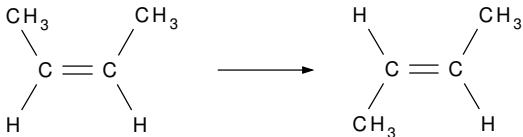
## Experimental determination of the Lindemann parameters

$$k_L = \frac{k_\infty [M]}{[M] + k_\infty/k_1}.$$

$$\therefore \frac{1}{k_L} = \frac{1}{k_\infty} + \frac{1}{k_1} \frac{1}{[M]}$$

A plot of  $k_L^{-1}$  vs  $[M]^{-1}$  therefore allows us to recover  $k_\infty$  and  $k_1$ .

Example: cis-trans isomerization of 2-butene at 740 K

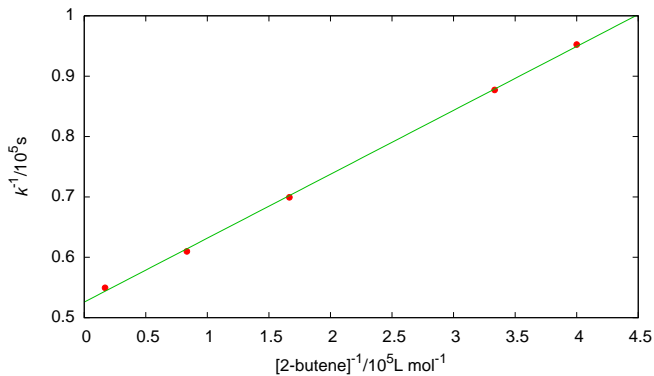


$[2\text{-butene}]/10^{-5}\text{ mol L}^{-1}$	0.25	0.3	0.6	1.2	5.9
$k/10^{-5}\text{ s}^{-1}$	1.05	1.14	1.43	1.65	1.82

Note: The theory is the same even if the “bath gas” is the reactant itself.

# Example: cis-trans isomerization of 2-butene at 740 K

(continued)



# Example: cis-trans isomerization of 2-butene at 740 K

(continued)

$$\text{slope} = 0.106 \text{ mol s L}^{-1}$$

$$\therefore k_1 = \frac{1}{\text{slope}} = 9.4 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$\text{intercept} = 0.53 \times 10^5 \text{ s}$$

$$\therefore k_\infty = 1.9 \times 10^{-5} \text{ s}^{-1}$$

## The value of $k_1$

- If we vary the temperature, we can get the preexponential factor and activation energy corresponding to  $k_1$ .
- We might guess that  $k_1$  (rate constant for  $A + M \rightarrow A^* + M$ ) is collision limited.  
We should therefore be able to predict the pre-exponential factor from collision theory.

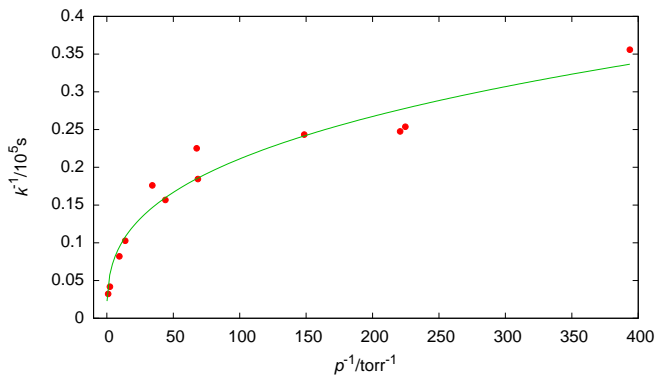
## Collision-theory preexponential factor for the collisional activation of cyclopropane at 760 K

- The hard-sphere radius of cyclopropane is 2.2 Å.
- $\sigma = \pi(2r)^2 = 6.1 \times 10^{-19} \text{ m}^2$
- The mean relative speed of cyclopropane molecules is

$$\begin{aligned}\bar{v}_r &= \sqrt{\frac{8RT}{\pi\mu_m}} \\ &= \sqrt{\frac{8(8.314472 \text{ J K}^{-1}\text{mol}^{-1})(760 \text{ K})}{\pi(70.134 \times 10^{-3} \text{ kg mol}^{-1})}} \\ &= 479 \text{ m s}^{-1}.\end{aligned}$$

- $A_{\text{ct}} = \sigma\bar{v}_rL = 1.75 \times 10^8 \text{ m}^3\text{mol}^{-1}\text{s}^{-1} \equiv 1.75 \times 10^{11} \text{ L mol}^{-1}\text{s}^{-1}$
- Experimental value:  $9 \times 10^{18} \text{ L mol}^{-1}\text{s}^{-1}$

## Curved Lindemann plots



Lindemann plot for the decomposition of cyclobutane to ethene at 449 °C

Source: Butler and Ogawa, *JACS* **85**, 3346 (1963).



## Summary: the two problems with Lindemann theory

- 1 The rate constant  $k_1$  exceeds the collision theory value, which should be an upper limit according to the theory studied so far.
- 2 Plots of  $k^{-1}$  vs  $p^{-1}$ , which should be straight, deviate from linearity at low pressures.