

Unimolecular Reactions

John W Daily

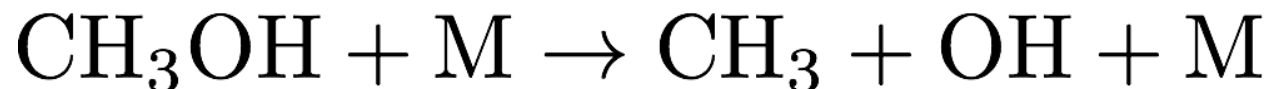


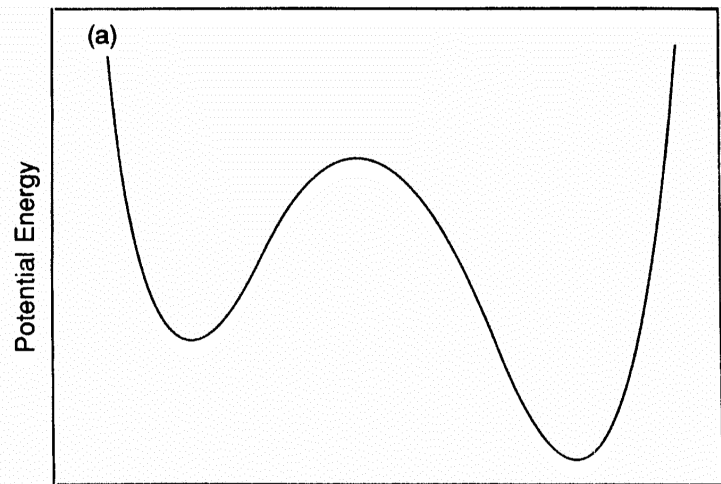
Unimolecular Reactions

- These are reactions involving changes for only one reactant.



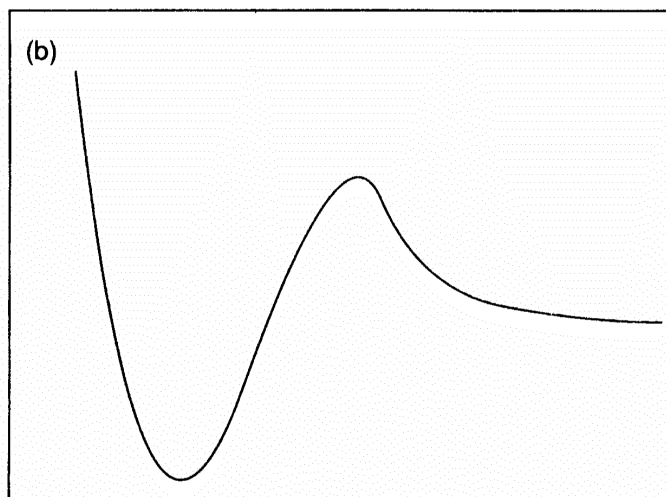
- The reaction could be isomerization, dissociation with an energy barrier on both directions, or dissociation with a barrier only for the dissociation.
- Example:



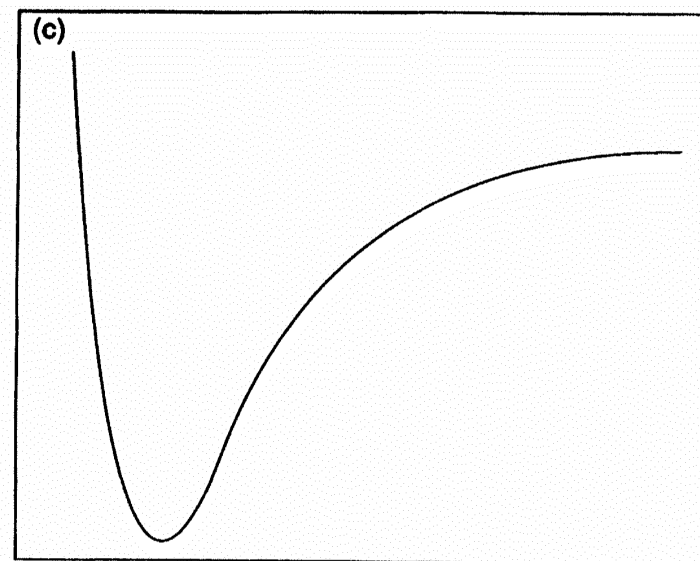


Isomerization

Dissociation
With barrier to
Reverse reaction



Dissociation without barrier
To reverse reaction



Lindemann-Hinshelwood Theory

- The theory proposes that



- It assumes that the reverse reaction is “strong,” occurring at the gas kinetic rate and that A^* is not formed from the products.
- If the steady state approximation is applied to A^* , then the overall rate becomes:

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



- Note that the rate is first order at high pressures as $[M] \rightarrow \infty$
- The high pressure limit is:

$$k_{uni} \rightarrow k_{\infty} = \frac{k_1 k_2}{k_{-1}} \quad \text{Rate} = k_{uni} [A]$$

- The low pressure limit is:

$$k_{uni} \rightarrow k_0 = k_1 [M] \quad \text{Rate} = k_0 [A] [M]$$



- The unimolecular rate constant can be written

$$k_{uni} = \frac{k_{\infty}}{1 + k_{\infty}/k_1[M]}$$

- where k_{∞} is the rate in the high pressure limit.
- The pressure at which $k_{uni} / k_{\infty} = 1/2$ is called $p_{1/2}$. Thus,

$$p_{1/2} \propto [M]_{1/2} = k_{\infty}/k_1$$



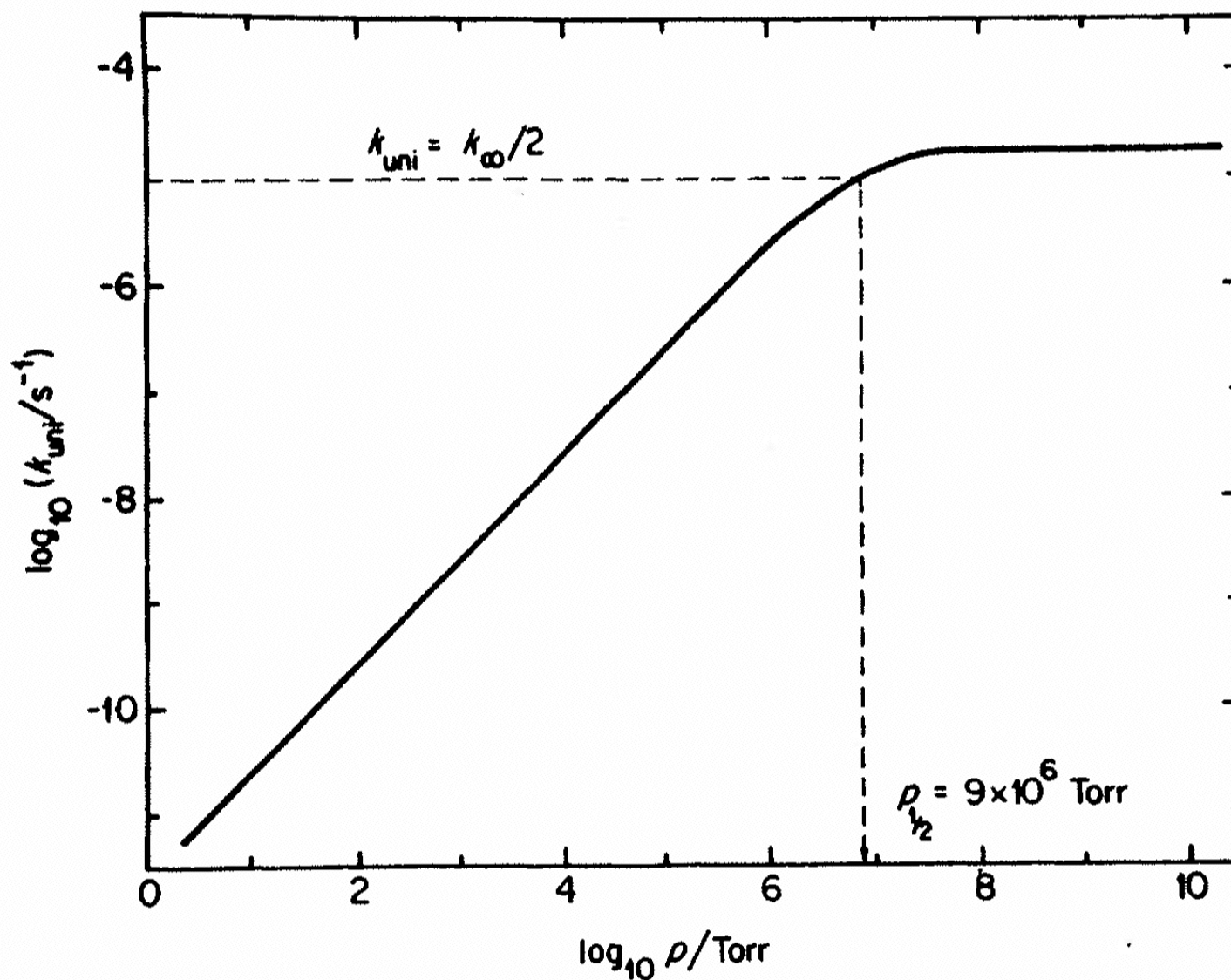


FIGURE 11-7 Theoretical Lindemann plot for *cis*- $\rightarrow$ *trans*-but-2-ene at 469°C. [Adapted from P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (New York: Wiley-Interscience, 1972). Reproduced with permission of John Wiley and Sons Limited.]



Example Reaction

- `falloff_reaction('C3H8 (+ M) <=> C2H5 + CH3 (+ M),
kf=[1.290000e+37, -5.84, 97387.67],
kf0=[5.640000e+74, -15.74, 98718.93],
efficiencies='AR:0.7 C2H6:3.0 CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0',
falloff=Troe(A=0.31, T3=50.0, T1=3000.0, T2=9000.0))`
 - Here k_f is the high pressure limit reaction rate constant, and k_{f0} the low pressure limit.
 - Of course it matters what M is, hence efficiencies for different M's are provided.
 - And the Lindemann theory isn't that great. Jurgen Troe developed a better functional form for the transition between the two limits, and the parameters for this are given.

