LINDEMANN THEORY AND IT'S LIMITATIONS (1/2)

Lindemann Theory (LT) provides a framework for understanding unimolecular reactions, e.g: $A \rightarrow P$

Obviously A can't just fall apart into P. It needs to overcome some activation barrier. This energy is gained by collisional excitation:

① $A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$, where M is a third body → this could be anything. An inert gas, or another A molecule.

(Ground state A; excited A)

The excited A then falls apart:

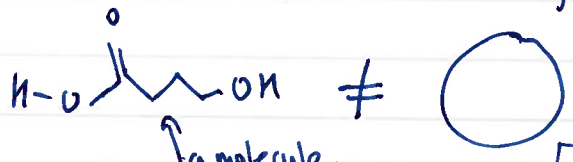
② $A^* \xrightarrow{k_2} P$, so overall rate $= \frac{d[P]}{dt} = k_2[A^*]$ (this is found using the SSA)

SSA shows us that $[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$, and then rate $= k_2\left(\frac{k_1[A][M]}{k_{-1}[M] + k_2}\right)$

Great! Now we can analyse the kinetics at high and low [M] by changing the denominator (@ high [M], $k_{-1}[M] + k_2 \simeq k_{-1}[M]$)
(@ low [M], $k_{-1}[M] + k_2 \simeq k_2$)

This is all great and probably useful for an exam. But there are problems with LT:

Problem #1: LT assumes ① is governed by SCT (simple collision theory). Unfortunately molecules are complicated and aren't just hard spheres.



Problem #2: Excited molecules aren't necessarily activated molecules. Lots of times, a molecule needs excitation in a specific mode to be able to undergo a reaction. Just being hot and excited and all vibrating doesn't mean you are usefully reactive!

Running really fast won't help you win a race if you're running in the wrong direction!

TUNE INTO PART 2/2 FOR THE SOLUTIONS!