Unimolecular Reactions- Lindemann-Henshelwood Mechanism

How do first order reactions occur?

$$A + A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A + A^* \qquad A^* \xrightarrow{k_1} B + C$$

where A* is an activated molecule

$$\frac{d[A^*]}{dt} = k_2[A]^2 - k_{-2}[A^*][A] - k_1[A^*] = 0$$

$$k_2[A]^2 = k_{-2}[A^*][A] + k_1[A^*]$$

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

$$\frac{d[B]}{dt} = k_1[A^*] = \frac{k_1 k_2[A]^2}{k_{-2}[A] + k_1}$$

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when $k_1 << k_{-2}$: slow unimolecular reaction from activated reactant

$$\frac{d[B]}{dt} = \frac{k_1 k2}{k_{-2}}[A]$$

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when $k_{-2} << k_1$: slow deactivation

$$\frac{d[B]}{dt} = k_2[A]^2$$

Test by measuring pressure dependence:

at low pressure: A + A* collisions unlikely so get slow deactivation:
should see second order reaction

at high pressure: A + A* collisions likely so deactivation is fast:
unimolecular step is the slow step, should see first order