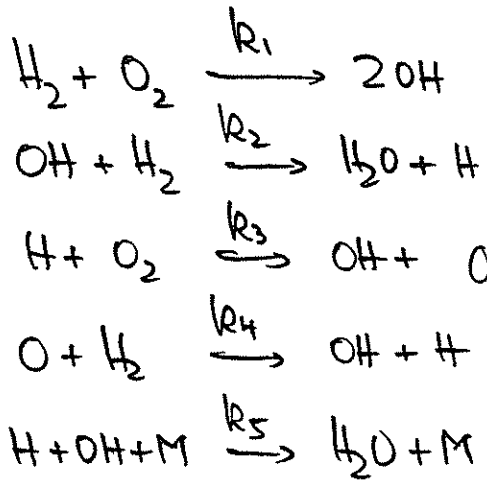


Global rxn vs.

[...often only the important steps...]



$$k_1 = 10^{12} \exp\left(-\frac{39}{RT}\right)$$

$$k_2 = 10^{13.8} \exp\left(-\frac{5.9}{RT}\right)$$

$$k_3 = 2.2 \times 10^{14} \exp\left(-\frac{16.5}{RT}\right)$$

$$k_4 = 1.1 \times 10^{13} \exp\left(-\frac{9.4}{RT}\right)$$

$$k_5 \approx 10^{17} \frac{\text{cm}^6}{\text{mol}^2 \cdot \text{s}}$$

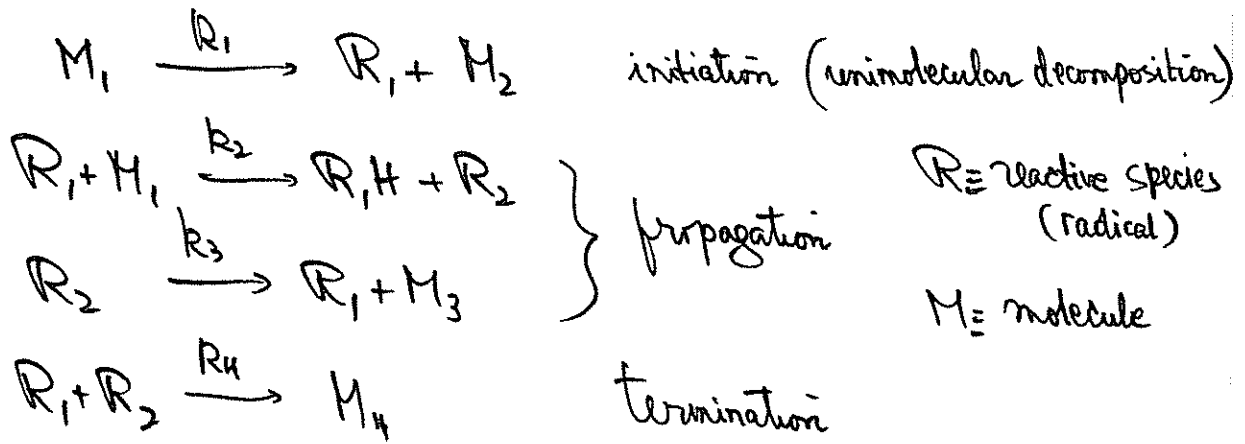
$\frac{\text{cm}^3}{\text{mol} \cdot \text{s}}$

Which steps are initiation/propagation/termination, and why?

$$\Rightarrow \frac{d[H_2O]}{dt} = 2k_2 [O_2][H_2] \left( \frac{k_1}{k_2} + \frac{k_3}{k_5[M]} \right) \quad (\text{Show!})$$

OK, SSA for all intermediates!  
(highly reactive)

(b) An elegant explanation for first-order kinetics of many decomposition rxns, including the chain rxn mechanism, is the Rice-Herzfeld mechanism



$R \equiv$  reactive species (radical)  
 $M \equiv$  molecule

$$\text{SSA: } [R_1] = \left( \frac{k_1 k_3}{2k_2 k_4} \right)^{0.5} \quad - \frac{d[M_1]}{dt} = k_1 \left[ 1 + \frac{k_2 k_3}{2k_1 k_4} \right]^{0.5} [M_1]$$

= chain length OK!