How do termolecular reactions proceed?

- two-step mechanism
  
  (1) \( A + B \rightarrow \{AB\}^* \)
  
  (2a) \( \{AB\}^* + M \rightarrow AB \)
  
  (2b) \( \{AB\}^* \rightarrow A + B \)

- Rate for intermediate species \( \{AB\}^* \)?
  
  \[
  \frac{d\{AB\}^*}{dt} = k_1 [A][B] - (k_{2a} [M] + k_{2b}) \{AB\}^* = 0
  \]
  
  \Rightarrow \{AB\}^* = \frac{k_1 [A][B]}{k_{2a} [M] + k_{2b}}

- Re-substitution into rate for (2a):
  
  \[
  \frac{d[AB]}{dt} = k_1 k_{2a} [M] / (k_{2b} + k_{2a}[M]) [A][B]
  \]
  
  with pseudo first order \( k' = k_1 k_{2a} [M] / (k_{2b} + k_{2a}[M]) \)
Lifetimes, SS, Fate of ·OH

- *Lifetimes* are defined as the e-folding time of a species’ concentration over its loss rate in the atmosphere:

  Example: \( \text{CO} + \cdot\text{OH} \rightarrow \text{H} \cdot + \text{CO}_2 \)

  \[
  \frac{d[\text{CO}]}{dt} = -k_{\text{CO+OH}} [\text{CO}][\cdot\text{OH}] \approx -k'_{\text{OH}} [\text{CO}]
  \]

  assuming \( \cdot\text{OH} \) is constant, i.e. in *Steady State (SS)*

  Lifetime \( = \tau = [\text{CO}] / (k_{\text{OH}}[\cdot\text{OH}][\text{CO}]) = 1 / (k_{\text{OH}}[\cdot\text{OH}]) \)

- The lifetimes of most molecules in the atmosphere are determined by their \( k_{\text{OH}} \)!

- SS can be assumed for all short-lived species, i.e. essentially all radicals

  SS: production rate = loss rate
OH production and loss

Main production pathway in 90% of the atmosphere:

(3b) \( \text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2 \cdot \text{OH} \)

Main loss pathways in 95% of the atmosphere:

(5) \( \text{CO} + \cdot \text{OH} \rightarrow \text{H} \cdot + \text{CO}_2 \)
(6) \( \text{CH}_4 + \cdot \text{OH} \rightarrow \cdot \text{CH}_3 + \text{H}_2\text{O} \)

⇒ knowledge of \( \cdot \text{OH} \), CO, and CH\(_4\) sources and sinks in the atmosphere is critical!!

FIGURE 11.49 Diurnal variation of OH measured using LIF (○) and DOAS (●) in a rural area in Germany on the (a) 16th and (b) 17th of August 1994. (Adapted from Hofzumahaus et al., 1998.)
Other sources of ·OH, “HOₓ”

- HOₓ is defined as the sum of ·OH and HO₂⁻.
- HO₂⁻ is formed in both CO and CH₄ oxidation e.g. in H· + O₂ + M → HO₂⁻ + M
- fast inter-conversion of HOₓ species occurs via
  (7) HO₂⁻ + O₃ → ·OH + 2 O₂
  (8) ·OH + O₃ → HO₂⁻ + O₂
  (9) HO₂⁻ + NO → ·OH + NO₂
  (10) every time ·OH reacts with a VOC or H₂
- Hence, every time either a net ·OH or HO₂⁻ radical is formed, this is called a HOₓ source