Example Questions involving Gas Phase Kinetics

1. Trichloroethylene (TCE) is an example of a volatile organic compound. Its bimolecular reaction with **OH** has $k = 2.3 \times 10^{-12}$ cm^3 molec^{-1} s^{-1} at 300 K. Estimate the *half-life* and *residence time* (lifetime) of TCE in the atmosphere if the average concentration of **OH** remains fairly constant at 2.0×10^6 molec cm^3.

[*Ans: $t_{1/2}$ (TCE) = 42 hr; τ(TCE) = 60 hr*]

2. Assume the following reaction is an *elementary* process.

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

a) Write the rate law for this reaction.
b) A sample of air at 290 K is contaminated by 1.0 ppm$_v$ of **NO**. Under these conditions, can the rate law be simplified?
c) Under the conditions described in b), the half-life of **NO** has been estimated at 100 hrs. What would the half-life be if the initial **NO** concentration were 12 ppm$_v$?

[*Ans:* *a) rate = k [**NO**]^2 [**O_2**]*
*b) rate = k' [**NO**]^2, where k' = k [**O_2**] is a pseudo second order rate constant*
*c) $t_{1/2}$ (**NO**)= 8.3 hr]*

3. The reaction

$$\mathbf{O}(g) + \mathbf{O_2}(g) + M \rightarrow \mathbf{O_3}(g) + M$$

has a rate constant = 1.1×10^{-33} cm^6 $molecule^{-2}$ s^{-1} at 220K (stratosphere).
a) What is the rate of reaction if P_T = 0.010 atm and the concentration of atomic oxygen is 2.1×10^{-4} ppm_v.
b) Calculate the *pseudo*-first order rate constant for this reaction and the *lifetime* (i.e., residence time) for of **O**(g) under these conditions.

[*Ans: a) rate = 1.8×10^9 molec cm^{-3} s^{-1}*
*b) k' = k [$\mathbf{O_2}$] [M] = 25.7 s^{-1}; τ(**O**) = 39 ms*]

4. What is the *lifetime* (i.e., residence time) of atomic oxygen in the troposphere if its major sink is the reaction

$$\mathbf{O}(g) + \mathbf{O_2}(g) + M \rightarrow \mathbf{O_3}(g) + M$$

Assume 15ºC, 1.00 atm and that $k = 6.0 \times 10^{-34} (T/300)^{-2.3}$ cm^6 $molecule^{-2}$ s^{-1}? Compare this result with that found in Q3, above.

[*Ans: τ (**O**) = 11 μs; Note that atomic **O** is much shorter lived in the troposphere than the stratosphere due to the much greater number densities of at higher pressures.*]

5. A catalytic cycle that might have contributed to the formation of $\mathbf{H_2}$ from **H** in the early atmosphere of the Earth is

$$\mathbf{H} + \mathbf{CO} + M \rightarrow \mathbf{HCO} + M \qquad k_1$$
$$\mathbf{H} + \mathbf{HCO} \rightarrow \mathbf{H_2} + \mathbf{CO} \qquad k_2$$
$$\text{Net:} \quad 2\,\mathbf{H} \rightarrow \mathbf{H_2}$$

Calculate the *steady state* concentration of the radical **HCO**, if the concentrations of **CO** and **M** were 1.0×10^{12} and 2.5×10^{19} molecules cm^{-3}, respectively and the magnitudes of the rate constants k_1 and k_2 are 1.0×10^{-34} cm^6 $molecules^{-2}$ s^{-1} and 3.0×10^{-10} cm^3 $molecules^{-1}$ s^{-1}, respectively.

[*Ans: [**HCO**] = 8.3×10^6 molec/cm^3*]