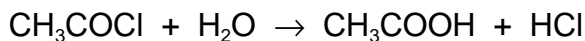


Chem 6 Homework Assignment 1 -- Kinetics 1

Zumdahl 5th ed. Ch. 15, exercises 11-17 (odd), 21, 25, 27, 31, 33, 43-47 (odd)
Zumdahl 5th ed. Ch. 21, exercises 15, 17

1. Consider the hydrolysis of acetyl chloride (CH_3COCl) to produce acetic acid (CH_3COOH) and hydrochloric acid (HCl). Note: water is the solvent.



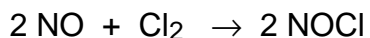
Experimentally the rate law is found to be

$$-d[\text{CH}_3\text{COCl}]/dt = k [\text{CH}_3\text{COCl}] [\text{H}_2\text{O}]$$

At the beginning of the reaction, the concentration of CH_3COCl is 0.10 M.

- At the beginning of the reaction, what is the concentration of H_2O ?
- If the reaction proceeds to completion what is the final concentration of H_2O ?
- If $k = 1.16 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, how long will it take for the concentration of CH_3COCl to be reduced to 0.05 M?

2. The gas phase reaction of nitric oxide, NO , with chlorine, Cl_2 , occurs according to the equation:



The experimental rate law is:

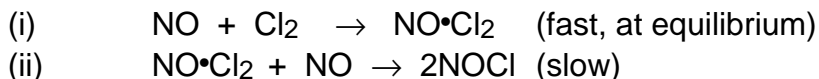
$$(1/2) d[\text{NOCl}]/dt = k [\text{NO}]^2 [\text{Cl}_2]$$

A possible reaction mechanism is:

- $2 \text{NO} \rightarrow \text{N}_2\text{O}_2$ (fast, at equilibrium)
- $\text{N}_2\text{O}_2 + \text{Cl}_2 \rightarrow 2 \text{NOCl}$ (slow)

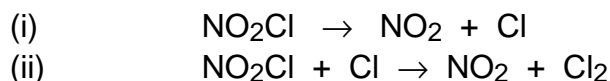
Identify the rate determining step (rds), show that this mechanism is consistent with the rate law, and express the experimental rate constant, k_{exp} , in terms of the rate constants for the elementary processes.

3. An alternative mechanism for the reaction considered in Problem #2 is:



Identify the rds, derive an expression for the rate of production of nitrosyl chloride, NOCl, and hence express the experimental rate constant, k'_{exp} , in terms of the rate constants for the elementary processes. Could kinetic data alone distinguish between the mechanism proposed in this problem and that proposed in Problem #2?

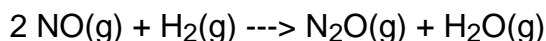
4. The mechanism for the decomposition $2 \text{NO}_2\text{Cl} \rightarrow 2 \text{NO}_2 + \text{Cl}_2$ is:



If step (i) is at equilibrium and fast relative to step (ii), show that the rate of disappearance of NO_2Cl is given by:

$$-d[\text{NO}_2\text{Cl}]/dt = 2 k_2 K [\text{NO}_2\text{Cl}]^2 [\text{NO}_2]^{-1}$$

5. The rate law of the reaction



is investigated at a certain temperature under pseudo-first-order conditions. The following two experiments are performed:

(1) 2.0 mol/L of NO is mixed with 0.010 mol/L of H_2 , and the time dependence of $[\text{H}_2]$ is determined, with the following results:

time(s)	$[\text{H}_2]$ (M)
0	1.0×10^{-2}
10	6.2×10^{-3}
20	3.8×10^{-3}
30	2.4×10^{-3}

(2) 2.0 mol/L of H_2 is mixed with 0.010 mol/L of NO, and the time dependence of $[\text{NO}]$ is determined, with the following results:

time(s)	$[\text{NO}]$ (M)
0	1.0×10^{-2}
1000	8.1×10^{-3}
2000	6.8×10^{-3}
3000	5.8×10^{-3}

Determine the rate law of the reaction and the value of the rate constant.