UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet IX

1. **NOTE:** For this question, the rate constants should be labelled with the number of the step in the proposed reaction mechanism, and any reverse steps be labelled similarly but with a prime. For example, see q. 1a.

(a) Derive the rate law for the decomposition of ozone in the reaction $2O_3(g) \rightarrow 3O_2(g)$ on the basis of the following proposed mechanism:

(1) O3 $\rightleftharpoons$ O2 + O (Rate constants: forward k_1, reverse k'_1)

(2) $O + O_3 \rightarrow 2O_2$ (Rate constant: k_2)

(b) (i) On the basis of the following proposed mechanism, account the experimental fact that the rate law for the decomposition $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is $v = k[N_2O_5]$.

(1) $2N_2O_5 \rightleftharpoons NO_2 + NO_3$

(2) $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$

(3) $NO + N_2O_5 \rightarrow 3NO_2$

(ii) A slightly different mechanism for the decomposition of N_2O_5 from that in (i) has also been proposed. It differs only in the last step, which is replaced by

(3) $NO + NO_3 \rightarrow 2NO_2$

Show that this mechanism leads to the same overall rate law.

(c) Consider the following mechanism for the thermal decomposition of R_2:

(1) $R_2 \rightarrow 2R$

(2) $R + R_2 \rightarrow P_B + R'$

(3) $R' \rightarrow P_A + R$

(4) $2R \rightarrow P_A + P_B$

where R_2, P_A and P_B are stable hydrocarbons and R and R' are radicals. Find the dependence of the rate of decomposition of R_2 on the concentration of R_2.

(d) The condensation reaction of propanone, $(CH_3)_2CO$, in aqueous solution is catalysed by bases, B, which react reversibly with propanone to form the carbanion $O_3H_5O^-$. The carbanion then reacts with a molecule of propanone to give the product. A simplified version of the mechanism is as follows:

(1) $AH + B \rightarrow BH^+ + A^-$

(2) $A^- + BH^+ \rightarrow AH + B$

(3) $A^- + AH \rightarrow$ product

where AH stands for propanone and A^- denotes its carbanion. Use the steady-state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

(e) Consider the acid-catalysed reaction:

(1) $HA + H^+ \rightleftharpoons HAH^+$ (k_1 forward, $k`_1$ reverse, both fast)

(2) $HAH^+ + B \rightleftharpoons BH^+ + AH$ (k_2, slow)

Deduce the rate law and show that it can be made independent of the specific term $[H^+]$.

(f) Consider the following chain mechanism:

(1) $AH \rightarrow A\cdot + H\cdot$

(2) $A\cdot \rightarrow B\cdot + C$

(3) $AH + B \rightarrow A\cdot + D$

(4) $A\cdot + B\cdot \rightarrow P$

Identify the initiation, propagation, and termination steps, and use the steady-state approximation to deduce that the decomposition of AH is first-order in AH.

(g) Consider the following chain mechanism:

(1) $A2 \rightarrow A\cdot + A\cdot$

(2) $A\cdot \rightarrow B\cdot + C$

(3) $A\cdot + P \rightarrow B\cdot$

(4) $A\cdot + B\cdot \rightarrow P$

Identify any initiation, propagation, retardation, inhibition, and termination steps, and use the steady-state approximation to deduce the rate law for the consumption of A_2.

(h) (i) Show that the pyrolysis of ethanal (acetaldehyde) exhibits the rate law:

$$CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g) \qquad \frac{d[CH_4]}{dt} = k[CH_3CHO]^{3/2}$$

given that the reaction proceeds according the Rice-Herzfeld mechanism, i.e.:

(a) $CH_3CHO \rightarrow \cdot CH_3 + \cdot CHO$

(b) $CH_3CHO + \cdot CH_3 \rightarrow CH_4 + CH_3CO\cdot$

(c) $CH_3CO\cdot \rightarrow \cdot CH_3 + CO$

(d) $\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3$

and hence deduce the rate of disappearance of ethanal.

(ii) Classify steps (a) - (d) according to initiation, propagation, *etc.*

(i) Although the stoichiometric equation for the reaction between hydrogen and bromine to give HBr looks very simple, the rate law is very complicated, i.e.:

$$H_2(g) + Br_2(g) \rightarrow 2HBr \qquad \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]}{[Br_2] + k'[HBr]}$$

The proposed mechanism for this reaction is as follows:

$$Br_2 + M \rightarrow Br\cdot + Br\cdot + M$$
$$(M = Br_2 \text{ or } H_2)$$

$$Br\cdot + H_2 \rightarrow HBr + H\cdot$$
$$H\cdot + Br_2 \rightarrow HBr + Br\cdot$$
$$H\cdot + HBr \rightarrow H_2 + Br\cdot$$
$$Br\cdot + Br\cdot + M \rightarrow Br_2 + M^*$$

where the third body M in the final step removes the energy of recombination.

(i) Classify the above steps as initiation, propagation, etc.
(ii) Prove that if the formation of HBr proceeds though this mechanism, then the rate law is indeed as stated above.

2. (a) Discuss methods for measuring the rates of chemical reactions.

(b) Write brief notes on:
(i) The variation of reaction rates with changes in temperature;
(ii) The verification of the Arrhenius equation through the collision theory
(iii) The relationship between the activation energy of different steps in a series consecutive reactions and the overall rate constant.
(iv) The variation of the rate constant of a reaction between ions with the ionic strength of the solution.