A First Course on Kinetics and Reaction Engineering

Example 9.2

Problem Purpose

This problem illustrates the generation of a rate expression for a non-elementary reaction where charged species are involved in the mechanism and the conservation of charge must be used.

Problem Statement

The macroscopically observed hydrolysis of methyl acetate is given in equation (1). The reaction is acid catalyzed. Suppose the mechanism given in equations (2) through (5) actually takes place and that step (4) is rate-determining. Generate a rate expression for the overall, macroscopically observed reaction.

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOH + CH_3OH \tag{1}$$

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^- \tag{2}$$

$$CH_3COOCH_3 + H_3O^+ \rightleftarrows CH_3COOCH_4^+ + H_2O \tag{3}$$

$$CH_3COOCH_4^+ + H_2O \rightarrow CH_3COOH_2^+ + CH_3OH \tag{4}$$

$$CH_3COOH_2^+ + H_2O \rightleftarrows CH_3COOH + H_3O^+ \tag{5}$$

Problem Analysis

This problem asks us to generate a rate expression from a reaction mechanism. There is a rate-determining step in the mechanism, so the rate of the macroscopically observed, non-elementary reaction will equal the rate of the rate determining step. The rate expression for that step will likely involve concentrations of reactive intermediates that need to be eliminated. This can be accomplished by writing equilibrium expressions for the other steps in the reaction mechanism along with an expression that requires conservation of electrical charge.

Problem Solution

We begin by checking that there is a linear combination of the mechanistic steps that adds up to give the overall reaction. We can see by inspection that if we add steps (3), (4) and (5) together, the result is reaction (1), so the mechanism is consistent with the macroscopically observed stoichiometry.

Since step (4) is the rate-determining step (RDS), the overall rate is equal to the forward rate of step (4) as given in equation (6).

$$r_1 = r_{4,f} = k_{4,f}\left[CH_3COOCH_4^+\right]\left[H_2O\right] \tag{6}$$

Equation (6) is not acceptable because it contains the concentration of the reactive intermediate $CH_3COOCH_4^+$. In addition to $CH_3COOCH_4^+$, H_3O^+, Cl^- and $CH_3COOH_2^+$ are also reactive intermediates; they appear in the mechanistic steps, but not in the overall, macroscopically observed reaction. To eliminate the concentration of $CH_3COOCH_4^+$ from equation (6) first notice that all steps other than the

RDS, here steps (2), (3) and (5), are at quasi-equilibrium, so for them an equilibrium expression can be written.

$$K_2 = \frac{\left[H_3O^+\right]\left[Cl^-\right]}{\left[HCl\right]\left[H_2O\right]} \tag{7}$$

$$K_3 = \frac{\left[CH_3COOCH_4^+\right]\left[H_2O\right]}{\left[CH_3COOCH_3\right]\left[H_3O^+\right]} \tag{8}$$

$$K_4 = \frac{\left[CH_3COOH\right]\left[H_2O\right]}{\left[CH_3COOH_2^+\right]\left[H_3O^+\right]} \tag{9}$$

There are three quasi-equilibrium expressions, but there are four reactive intermediates. Another equation is needed, and that is the expression for the conservation of charge. For the present problem, expanding the summations in the conservation of charge equation leads to equation (10).

$$\sum_{\substack{p=\text{ all}\\\text{positively}\\\text{charged}\\\text{species}}} C_p q_p = \sum_{\substack{n=\text{ all}\\\text{negatively}\\\text{charged}\\\text{species}}} C_n \left|q_n\right|$$

$$\left[H_3O^+\right] + \left[CH_3COOCH_4^+\right] + \left[CH_3COOH_2^+\right] = \left[Cl^-\right] \tag{10}$$

We now have four equations (7) through (10) containing the concentrations of four reactive intermediates, and so the equations can be solved to get expressions for the intermediates. This can be done manually or with the use of symbolic algebra software. Doing so leads to the expression given in equation (11) for the concentration of $CH_3COOCH_4^+$. It will be left as an exercise for the interested reader to find expressions for the concentrations of the three other intermediates; only the concentration of $CH_3COOCH_4^+$ is needed to complete the problem.

$$\left[CH_3COOCH_4^+\right] = K_3 \frac{\left[CH_3COOCH_3\right]}{\left[H_2O\right]} \sqrt{\frac{K_2\left[HCl\right] - \dfrac{\left[CH_3COOH\right]}{K_5}}{\left[H_2O\right] + K_3\left[CH_3COOCH_3\right]}} \tag{11}$$

This can then be substituted into the rate expression, equation (6), producing the desired result.

$$r_1 = k_{4,f} K_3 \left[CH_3COOCH_3\right] \sqrt{\frac{K_2\left[HCl\right] - \dfrac{\left[CH_3COOH\right]}{K_5}}{\left[H_2O\right] + K_3\left[CH_3COOCH_3\right]}} \tag{12}$$

If water is the solvent for the system, then its concentration is expected to be large and constant. As a consequence, the second term in the denominator is likely to be small compared to the water concentration, and so can be dropped.