CSTR study:
The reaction of t-butyl chloride and water

Introduction

The reaction between tert-Butyl chloride (t-butyl chloride) and water is investigated at different conditions. The experiment is conducted in a CSTR reactor. The conversion level is monitored with a pH-meter. The reactants are t-butyl chloride in methanol (tBC/MeOH) and water in methanol (H_2O/MeOH). The temperature and residence time are varied while the concentrations of tBC and water in the feedstock are kept constant.

For all reaction conditions the tBC conversion and forward rate constant is determined (assuming it's an irreversible reaction). The activation energy is also determined.

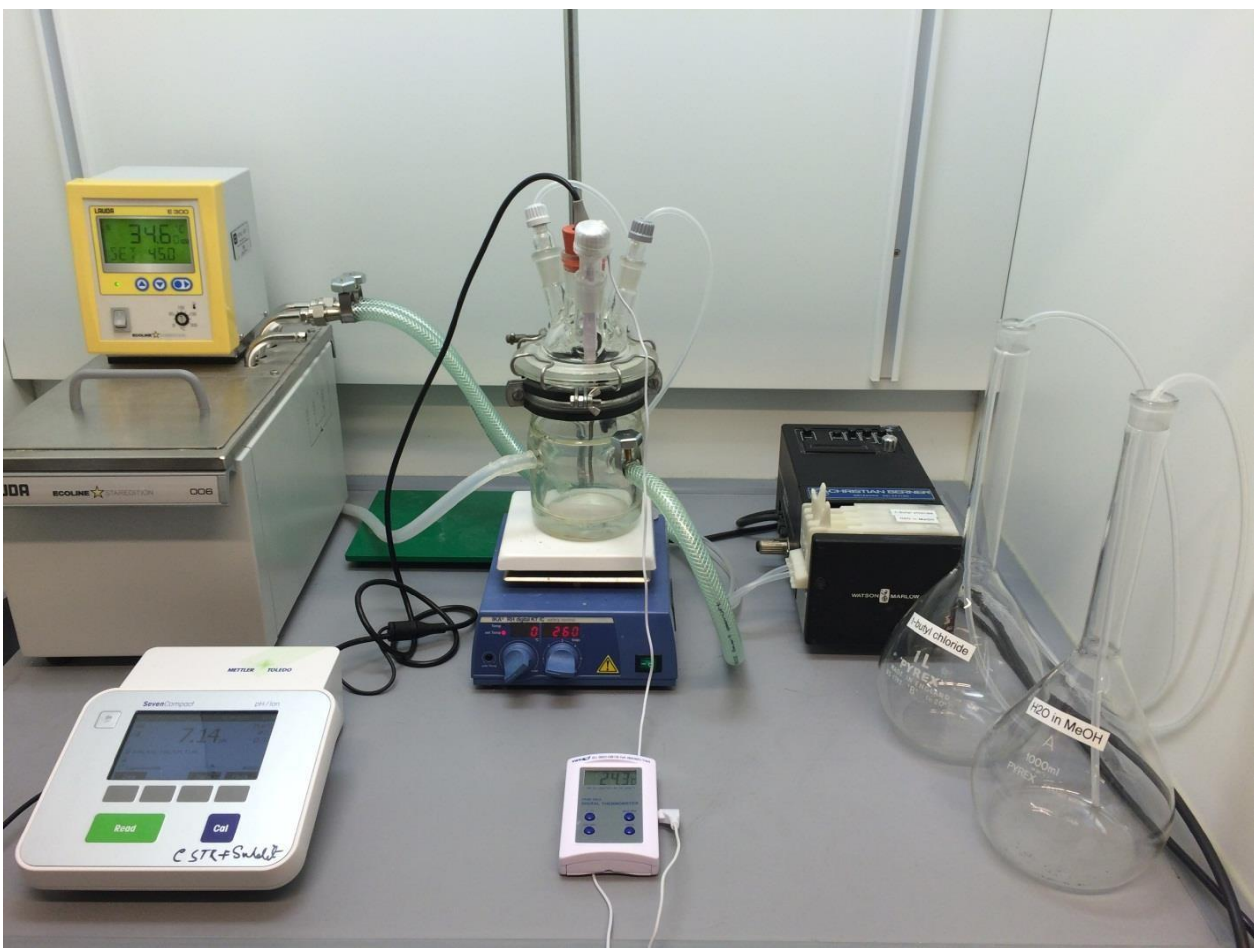

Figure 1 – CSTR experimental setup

Theory

Water and t-butyl chloride react according to the following equations:

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + HCl \tag{1}$$

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_2CCH_2 + H_3O^+Cl^- \tag{2}$$

Both the substitution (equation 1) and the elimination (equation 2) pathways occur in competition with each other. Figure 2 demonstrates the mechanism of t-butyl chloride hydrolysis. The generation of carbocation from t-butyl chloride is the rate limiting step, and the reaction is therefore a first order reaction where the rate expression can be written as:

$$-r = kC_{t-BC} \tag{3}$$

"k" is the reaction rate constant. According to Arrhenius equation:

$$k = Ae^{\frac{-E}{RT}} \tag{4}$$

Where, "A" is pre-exponential factor, "E" is the activation energy [J/mol], "R" is the gas constant which is 8.314 [J/(K.mol)] and "T" is the absolute temperature [K].

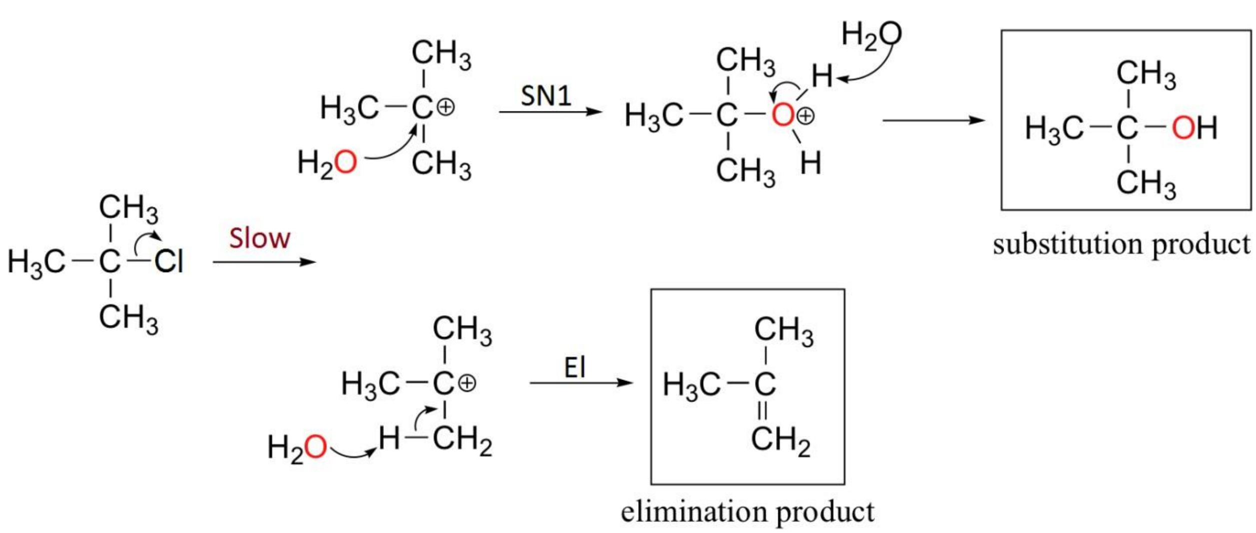

Figure 2- Mechanism of t-butyl chloride hydrolysis

Calculations

Figure 3 shows a schematic diagram of the CSTR setup. Mass balance can be written as follow:

$$v_f(C_i)_f - v_p(C_i)_p = -rV \tag{5}$$

Where "V" is the reaction volume (which is 207 mL) and "v" is the volumetric flow rate of feed or product stream. Under steady-state conditions (v_f=v_p=v_0), mass balance can be simplified as:

$$(C_i)_f - (C_i)_p = -r\frac{V}{v_0} = -r\tau \tag{6}$$

"τ" is the mean residence time. Inserting the expression for the first order reaction (equation 3) gives:

$$(C_i)_f - (C_i)_p = k(C_i)_p\tau \tag{7}$$

Which can be solved for the rate constant:

$$k = \frac{1}{\tau}\left[\frac{(C_i)_f}{(C_i)_p} - 1\right] \tag{8}$$

The activation energy can be calculated from Arrhenius equation. Equation 4 can be re-written as:

$$\ln(k) = \ln(A) - \frac{E}{R}\left(\frac{1}{T}\right) \tag{9}$$

Plotting ln(k) versus 1/T will give a straight line with a slope of -E/R, from which the activation energy, "E" is calculated. The Arrhenius pre-exponential factor, "A", can also be found from this plot. For more theory, see Scott Fogler, Elements of Chemical Reaction Engineering.

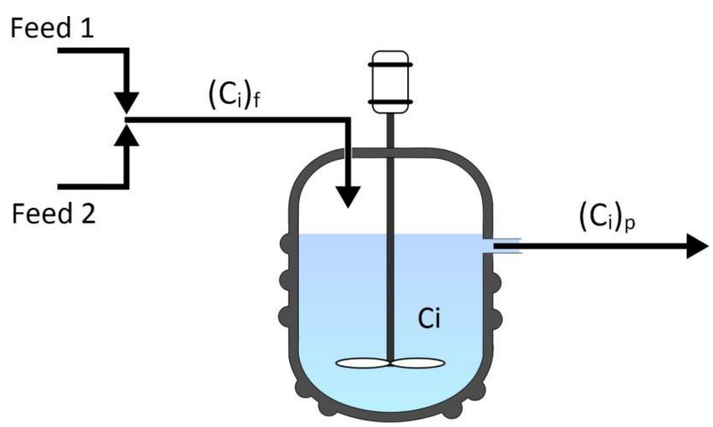

Figure 3 - Schematic diagram of the CSTR setup

Experiment

Each group will run the experiment at 6 different set of operating conditions (residence time and temperature). Pump speed and water bath temperature (which controls the reaction temperature) is changed according to the table 1.

Temperature in the water bath is always slightly different than the actual stabilized temperature in the reactor. Reactor may be insulated to reduce this difference. Calculations should be done according to the temperature measured inside the reactor.

Flow rates can be calculated from the pump's calibration curve. The calibration has been done already for set points above 50%. The final calibration curve will be provided after performing experiment.

Table 1 – Experimental conditions

Run	Water bath Temp.	Pump level	Group number	
			Even number	Odd number
1	30	80	✓	
2	30	60	✓	
3	35	80	✓	✓
4	35	60	✓	✓
5	40	80	✓	✓
6	40	60	✓	✓
7	45	80		✓
8	45	60		✓

Procedure

Prior to the experiment

- Read this guide thoroughly.
- Learn about the chemicals used in the experiment, especially on hazards and safety.
- Prepare the work plan (Maximum 2 pages, with an appendix not exceeding 2 pages) that should contain:
  1- Short theoretical introduction to the reaction system. Think about:
    - Which parameters must be measured and are necessary for calculations of conversion level, the rate constant and the activation energy?
    - How can the inlet and outlet concentrations, conversion level and consumption rate of tBC be calculated?

  2- Make a plan for the experiments; Calculate the amount of tBC, water and solvent (MeOH) based on 1000 mL reactant flasks. Calculate the expected total consumption of reactants and solvent (each run will take approximately 30 min).

  3- Include which values are going to be measured, tabulated and how these values are going to be used for further calculations. Sample calculation to be shown in the appendix.

   4- Explain how the measured values will be used to calculate kinetic parameters.
   5- What plots will you make? What information do you need to obtain from the plots?
- Read the Risk Assessment for the experiment and ask yourself various questions regarding hazards and safety.

Experiment

1- One solution of each reactant is prepared as follow:
   - H_2O in methanol, 35M;
   - t-butyl chloride in methanol, 0.025M.

Use measuring cylinders, pipettes and volumetric flasks as required, to prepare the solutions. Prepared solutions are stored in 1000/2000 mL volumetric flasks.

- ❖ NOTE! tBC is very volatile. It should be pipetted in ca.100 mL MeOH in order to minimize evaporation and get accurate measurement. KEEP THE COVER ON THE T-BUTYL CHLORIDE BOTTLE!!!
- ❖ NOTE! Wear gloves and safety goggles and work under a fume hood!

To avoid reaction between water and tBC outside the CSTR, two solutions are made in two separate flasks (marked) and then added to the CSTR through different tubes (marked) using a peristaltic pump.

Start-up

2- Make sure the waste container is not full.
3- Set the water bath temperature.
4- Connect the feed-hoses to the reactant solutions. To save time, fill the reactor with reactants with the maximum pump speed at the beginning of the first run.
5- Turn on the magnetic stirrer.
6- Re-calibrate the pH-meter using the available buffer solutions. The supervisor will help you. Wash the pH electrode with distilled water before putting it into the reactor.
7- Set the pump level.
8- The pH-value, the elapsed time and the temperature in the reactor should be recorded in the lab journal every 3 minutes as the reactor is approaching steady state, at each experimental condition. Here, pH value is used to indicate the reaction status. A reactor volume of **207 mL** can be used for estimating the necessary time to reach steady-state.

Subsequent runs

9- After reaching steady state, change the pump level and/or water bath temperature according to the given experimental conditions.
   - ❖ NOTE! DO NOT EMPTY THE REACTOR BETWEEN SUBSEQUENT RUNS.

10- Read out pH-values and temperature and record the elapsed time as described earlier.
11- If the reactant solution is running out, prepare new solution as described earlier

Shut-down

12- Turn off the water bath, turn off the magnetic stirrer and stop the pump.

13- Remove the pH-electrode and wash it with distilled water before putting it back into the storage solution.

14- Empty the reactor through the outlet hose at the end of the experiment. Never disconnect the water bath circulation and other connections from the reactor.

15- Clean and put back the glassware to where it was.

16- MAKE SURE THE LAB IS TIDY AND CLEAN, AND ALL ELECTRONIC EQUIPMENT IS TURNED OFF BEFORE LEAVING!!!

Use of lab journal

All lab works must be documented in the lab journal. It is important that the lab journal contains all essential data and observations from the experiment, including any possible problems with the apparatus. The lab journal in this experiment is a hardcover log book that will be present at the setup.

For data evaluation and report writing, make a copy of the lab journal after your experiment. A copy of this must be included in the report.

- NOTE! Make sure to return the journal and put it by the setup after making a copy.
- NOTE! DO NOT REMOVE any sheets from the journal!