

Hydrolysis of t-butyl chloride

CSTR-Study

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Abstract

This experiment was performed as part of TKP4110/TKP4106 Felleslab. The hydrolysis of tert-butyl chloride in a Continuously Stirred Tank Reactor (CSTR) was examined. The activation energy, Arrhenius pre-exponential factor and conversion level of the reaction was determined by varying temperature and residence time. The activation energy for the reaction was found to be $76.188 \text{ kJ mol}^{-1}$. The Arrhenius pre-exponential factor was found to be $e^{21.336}$.

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1 Theory

The reaction mechanism of t-butyl chloride hydrolysis is shown in figure 1.

The rate determining step of the mechanism is the formation of carbocations, thus the reaction is a first order unimolecular reaction. The form of the rate expression is given in (1.1),

$$-r = kC_{tBC} \quad (1.1)$$

where r is the reaction rate, k is a constant to be determined and C_{tBC} is concentration of t-butyl chloride. The reaction took place in a Continuous Stirred-Tank Reactor (CSTR). The level of conversion was monitored with a pH-meter.

The mass balance for the reactor can be written as (1.2).

$$v_f(C_i)_f - v_p(C_i)_p = -rV \quad (1.2)$$

where v_f is the volumetric flow of the feed, v_p is the volumetric flow of the product, $(C_i)_f$ and $(C_i)_p$ is the concentration of component i in the feed and the product(outlet). V is the total reactor volume. For steady state, $v_f = v_p = v_0$, and (1.2) can be written as (1.3).

$$(C_i)_f - (C_i)_p = -r \frac{V}{v_0} = -r\tau \quad (1.3)$$

where τ is the mean bed-residence time and v_0 is the start volume. τ is defined in (1.4), where Q_f the total feed volume calculated by (1.5).

$$\tau = \frac{V}{Q_f} \quad (1.4)$$

A calibration curve for Q_f as a function of the systems pump level P , is given as (1.5).¹

$$Q_f = 0.0025P^2 + 0.0768P + 2.6752 \quad (1.5)$$

Inserting (1.3) in to (1.1) gives:

$$(C_i)_f - (C_i)_p = k(C_i)_p\tau \quad (1.6)$$

The rate constant can then be found by rearranging (1.6) to (1.7)

$$k = \frac{1}{\tau} \left(\frac{(C_i)_f}{(C_i)_p} - 1 \right) \quad (1.7)$$

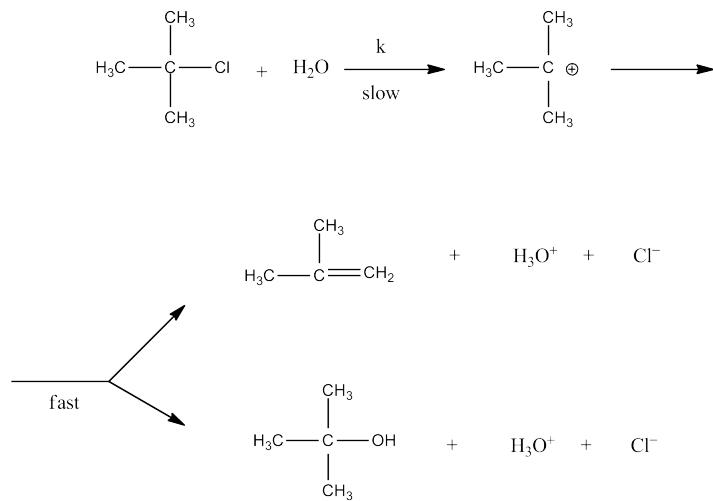


Figure 1: The figure shows the reaction mechanism for the hydrolysis of t-butyl chloride.

The Arrhenius equation is given as (1.8)¹

$$k = A e^{-\frac{E_a}{RT}} \quad (1.8)$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature and k the reaction rate constant. In linearized form (1.8) can be written as (1.9),

$$\ln(k) = \ln A - \frac{E_a}{RT} \quad (1.9)$$

Plotting $\ln(k)$ against $\frac{-1}{RT}$, will give a graph with a slope E_a . The pre-exponential factor can be determined from this plot.

Conversion level X is defined as the ratio of moles of a substance A reacted against the total moles of A fed to the reactor. For the system in this experiment, conversion level can be expressed as (1.10)

$$X = \frac{C_{tBC,0} - C_{tBC}}{C_{tBC,0}} = 1 - \frac{C_{tBC}}{C_{tBC,0}} \quad (1.10)$$

2 Experimental

2.1 Procedure

The feed solutions were prepared according to the calculations given in section A.1. Feed 1 contained 35M H_2O in $MeOH$ and feed 2 contained 0,025M t-Butyl Chloride.

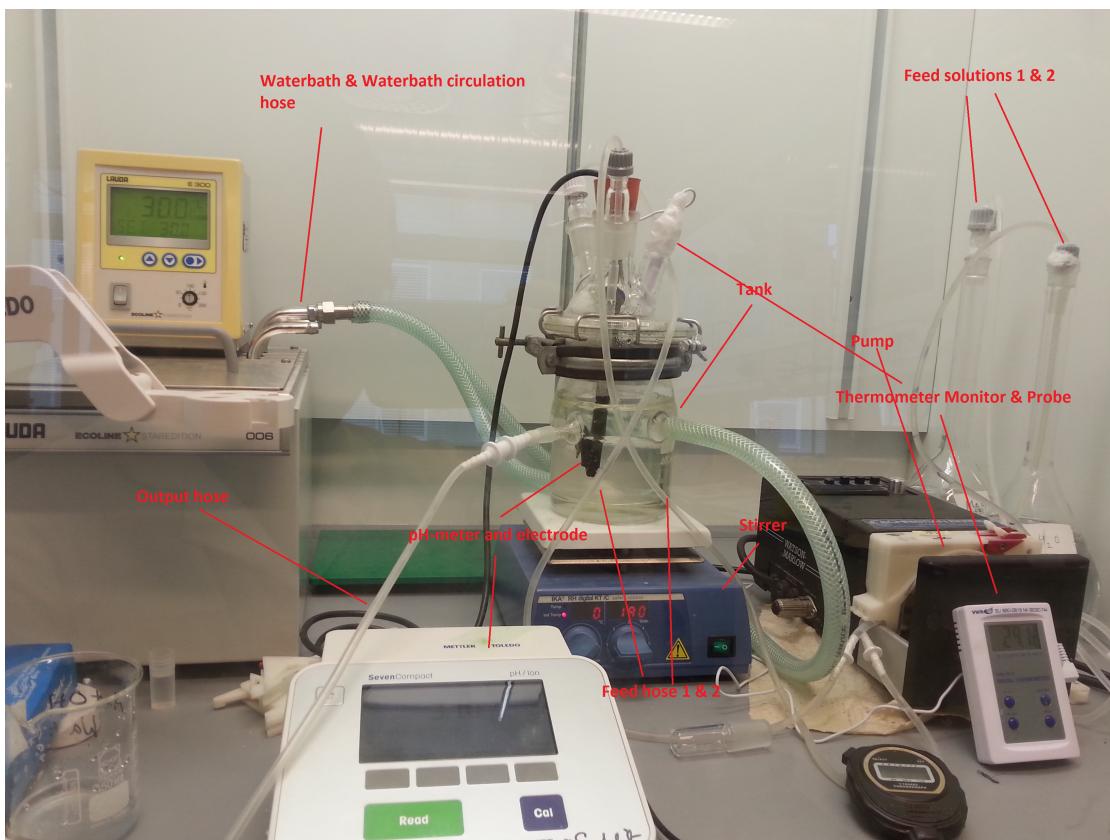


Figure 2: Photograph of the apparatus used in the experiment with vital parts labelled.

The temperature of the water bath were set and adjusted. The reactor was set up by connecting the feed hoses, in/out hoses, product container and pH-electrode. It was then filled quickly by using maximum pump level until the reactants reached the outlet hose. The stirrer were then turned on, and the reaction were monitored by noting the pH and temperature every 3 minutes as the reactor approached steady-state. A picture of the apparatus can be found in figure 2

When changing parameters of the experiment, the reactor was not emptied between runs. Temperature or pump level were adjusted and the system was left to reach steady-state, while pH and temperature were recorded as formerly described.

The reactant solutions was prepared in three batches in order to refill the feed solutions during the experiment. Refilling was done without interrupting the experiment by ensuring that no air was pumped into the feed hoses.

At the end of the experiment, the water bath and the stirring were turned

off and the pump were stopped. The pH-electrode was then removed and cleaned before it was put in the storage solution. The reactor was emptied through the product outlet. The circulation of the water bath was not disconnected.

The calibration curve for the pump is given as (2.1),

$$Q_f = 0,0025P^2 + 0,0768 * P + 2,6752 \quad (2.1)$$

where P is the level of the pump, and Q_f [ml/min] is the total feed volume rate (feed 1 + feed 2). The formula for Q_f (2.1) is used in table 1 to calculate the feed volumes needed for each run, with the assumption that one run lasts for 30 minutes. By summing the volumes of the last column, the necessary total feed volume is calculated to 1754,9 mL.

Table 1: The table shows calculated feed consumption and experimental parameters.

Run #	Temp WB [°C]	Pump level	Qf [mL min ⁻¹]	Feed Con- sumption [mL]
1	30	60	7,31	219,17
2	30	80	8,86	365,78
3	35	80	7,31	365,78
4	35	60	8,86	219,17
5	40	60	7,31	219,17
6	40	80	8,86	365,78

The temperature in the water bath will be slightly higher than in the reactor. This can be corrected by using (2.2), found from the script.¹

$$T_{bath} = 1,0352T_{reactor} - 1,1117 \quad (2.2)$$

3 Results

The results of the experiment are shown in the tables 3 to 5. The temperature was measured with both a pH-meter and a thermometer. An average of these temperatures are used in all calculations. The measurements and calculated averages can be seen in table 2

The regression line in figure 3 has the equation given in (3.1).

$$y = 76188X + 21,336 \quad (3.1)$$

Table 2: Measured temperatures and calculated averages for all runs.

Run #	Temp pH [°C]	Temp Therm [°C]	Average [°C]
1	29,2	29,1	29,15
2	29,5	29,1	29,3
3	33,8	33,4	33,6
4	34,1	33,7	33,9
5	38,6	38,2	38,4
6	38,2	37,8	38

Table 3: pH measurements at 30 °C waterbath temperature.

P60		P80	
Time [min]	pH	Time [min]	pH
0	3,63	0	3,02
3	3,4	3	3,05
6	3,3	6	3,05
9	3,22	9	3,09
12	3,18	12	3,09
15	3,13	15	3,09
18	3,11	18	3,09
21	3,09	21	3,09
24	3,08	24	3,1
27	3,05	27	3,09
30	3,02	-	-
33	2,99	-	-
36	2,98	-	-
39	3,03	-	-
42	2,98	-	-

Table 4: pH measurements at 35 °C waterbath temperature.

P60		P80	
Time [min]	pH	Time [min]	pH
0	2,91	0	3,04
3	2,9	3	2,97
6	2,87	6	2,95
9	2,85	9	2,98
12	2,84	12	2,96
15	2,83	15	2,95
18	-	18	2,94
21	-	21	2,93
24	2,84	24	2,93
27	2,83	27	2,93
30	2,83	30	2,93

Table 5: pH measurements at 40 °C waterbath temperature.

P60		P80	
Time [min]	pH	Time [min]	pH
0	2,79	0	2,66
3	2,74	3	2,68
6	2,72	6	2,71
9	2,71	9	2,71
12	2,7	12	2,73
15	2,69	15	2,72
18	2,68	18	2,73
21	2,67	21	2,73
24	2,66	24	2,73
27	2,66	27	2,73
30	2,66	-	-

Table 6: Calculated values for $\frac{-1}{RT}$ and $\ln(k)$ for all six runs. Temp WB is the temperature set on the waterbath, while Temperature is the average of the measured temperatures from the thermometer and pH-meter.

Temp WB [°C]	Pump level	Temperature [°C]	-1/RT	ln(k)
30	60	29,15	-3,98E-04	-9,02912
35	60	33,9	-3,92E-04	-8,64528
40	60	38,4	-3,86E-04	-8,18738
30	80	29,3	-3,98E-04	-8,88117
35	80	33,6	-3,92E-04	-8,48129
40	80	38	-3,87E-04	-7,95817

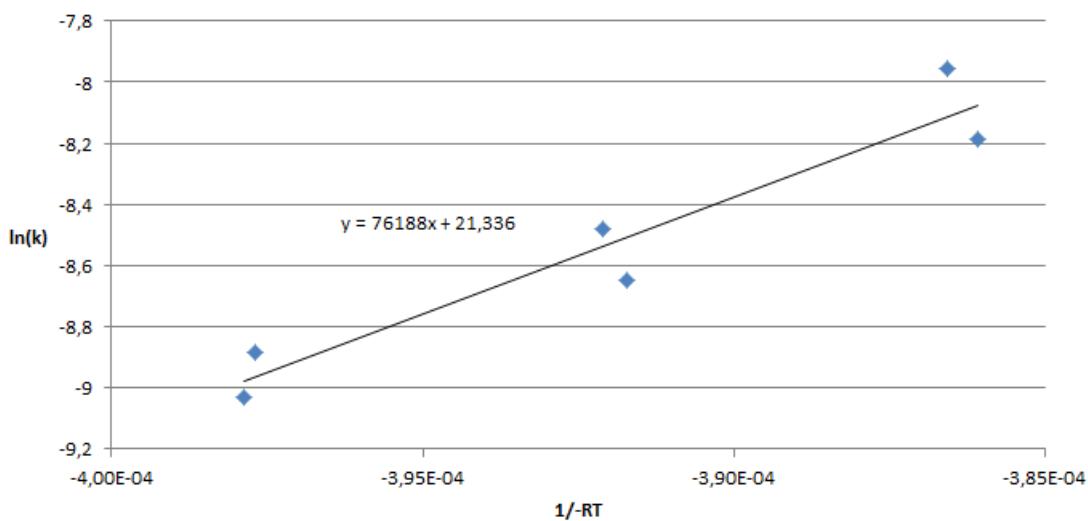


Figure 3: Plot of $\ln(k)$ against $\frac{-1}{RT}$ for all 6 runs. A regression line is drawn on the plot. The data for the plot can be found in table 6

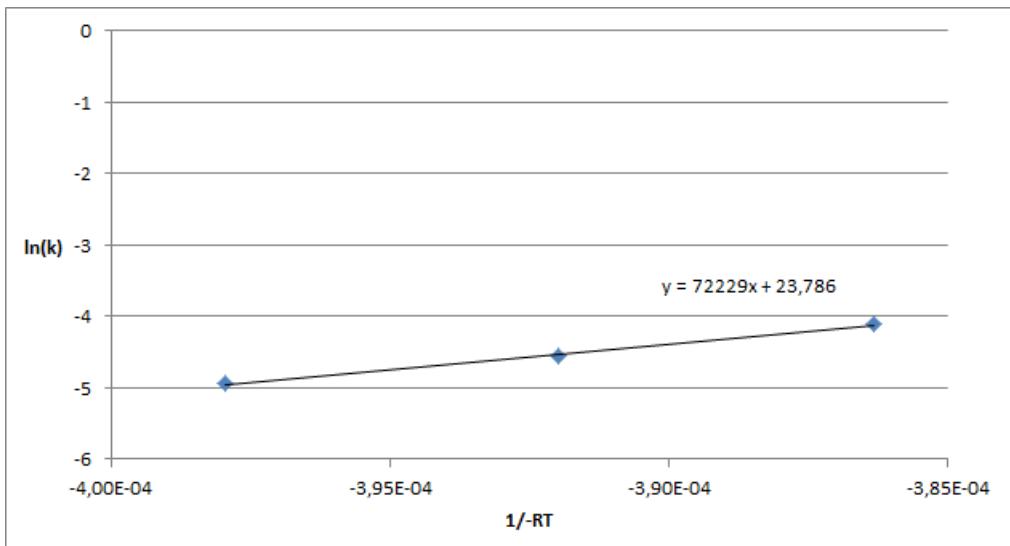


Figure 4: Plot of $\ln(k)$ against $\frac{1}{RT}$ for pump level 60. A regression line is drawn in the plot. The data for the plot can be found in table 6.

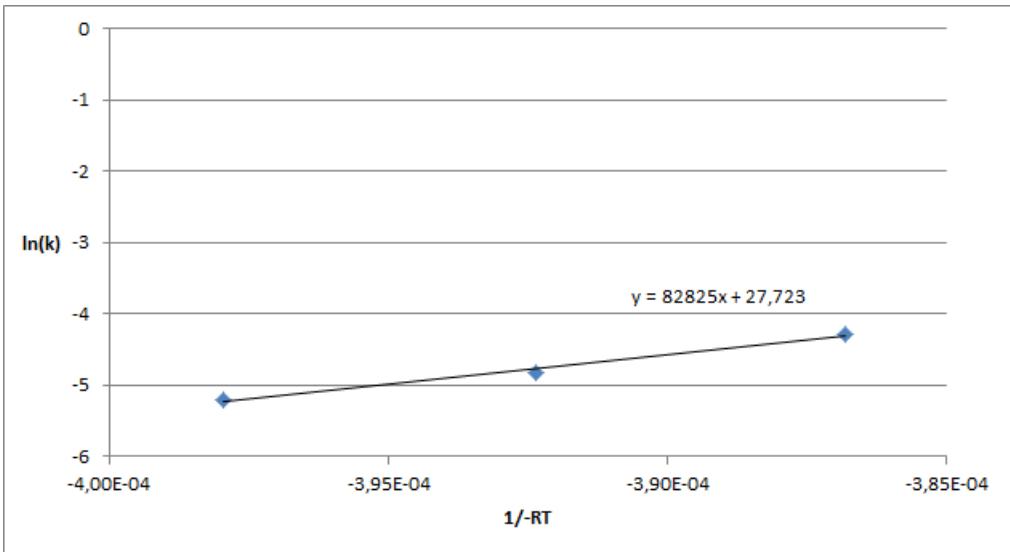


Figure 5: Plot of $\ln(k)$ against $\frac{1}{RT}$ for pump level 80. A regression line is drawn in the plot. The data for the plot can be found in table 6.

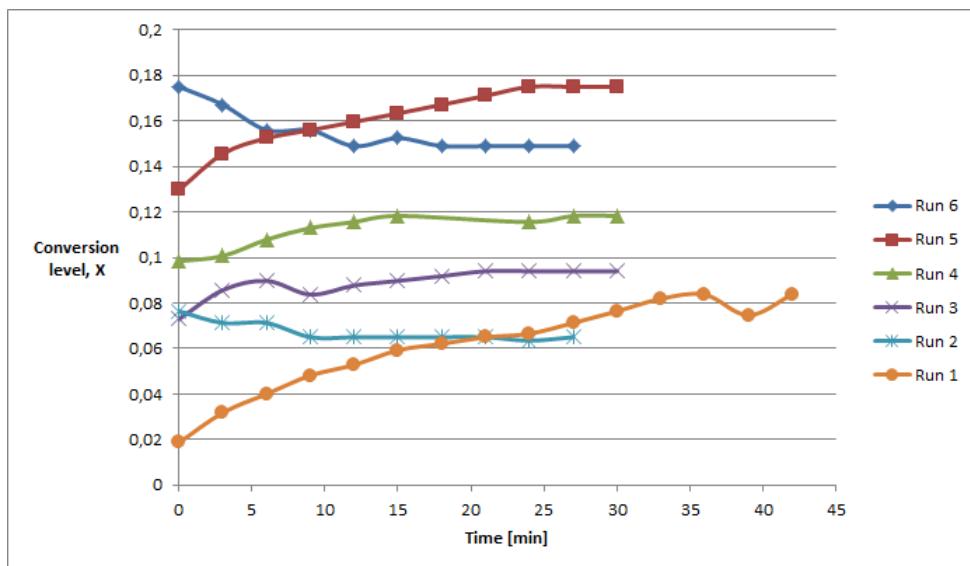


Figure 6: The figure shows a plot of conversion level X against time for all six runs. The data for the plot can be found in table 10.

Combining this expression and (1.9), the activation energy E_a and the pre-exponential factor A was found to be:

$$E_a = 76.188 \text{ kJ mol}^{-1}$$

$$A = e^{21.336}$$

A reference value for the activation energy of this reaction at reaction at 25 °C was found in an external article³ as $E_{ref} = 23150 \text{ calorie/mol} = 96.860 \text{ kJ mol}^{-1}$. The activation energy found from (3.1) deviates from the reference by 21.3 %.

Table 7: The table shows residence time, reaction constants and conversion level at steady state for all combinations of temperature and pressure level.

P	τ [min]	T [°C]	k [s ⁻¹]	X
60	12,712	29,15	7,14E-03	0,08377
60	12,712	33,9	1,05E-02	0,118329
60	12,712	38,4	1,66E-02	0,175021
80	8,340	29,3	5,43E-03	0,065026
80	8,340	33,6	8,10E-03	0,093992
80	8,340	38	1,37E-02	0,148967

4 Discussion

In the plot of $\ln(k)$ against $\frac{-1}{RT}$, figure 3, the points seem to align in two distinct lines. The separate plots for pump level 60 and 80 (figures 4 and 5) show that these lines correspond to the different pump levels, and that k increases with pump level. In the equation for k (1.7), it can be seen that k depends on τ , which in turn decreases with increased pump level.

From the plot in figure 3 the activation energy was found to be $76.188 \text{ kJ mol}^{-1}$, a value which deviates from the reference value by 21.3%. The reference value was given for 25°C , while this experiments was performed with higher temperatures. This may be a cause for some of the deviation. Other possible causes for error are discussed further down in this section.

The conversion level (shown in figure 6) flattens over time for all the runs, which indicates that the reaction approaches steady state after approximately 20 to 25 minutes. By comparing the conversion levels to their respective pump levels in table 7, it is seen that the runs with pump level 60 have higher conversion levels than the runs at pump level 80 at the same temperature at steady state. This seem reasonable as the residence time τ is dependent on the pump level. Lower pump level gives a higher residence time, and thus a higher conversion.

In table 2 it can be seen that the thermometers gave different measurements during the experiment. This may indicate a difference in accuracy or calibration between the thermometers. An other explanation for the difference in measurement could be that the solution is not ideally mixed as assumed. This could give a difference in measured temperature at two different points in the solution.

It is assumed that the reactor volume is 207 mL. This value is calculated from the height of output hose, and assumes a horizontal water level. The stirring gives the water a non-horizontal surface, where water level is higher towards the wall of the tank. This gives an actual reactor volume slightly lower than the assumed 207 mL. A difference in reactor volume will influence calculations of concentrations and can be a source of error in the experiment.

During the experiment it was observed that one of the feed containers was drained faster than the other. Bubbles of air was also observed in the feed hoses during the experiment, which gives a non-continuous reactant flow. As it is assumed a 1:1 relationship between the two reactant feeds and steady flows, this may be a cause for error.

The reactant solution was diluted in three batches. Some difference or error in measurement between these dilutions may give a difference in the initial concentration of t-Butyl Chloride, C_{tBC} . Considering the relatively large volumes of the feed solutions, minor differences in measurements during

dilution will probably not be a large influence on the results.

5 Conclusion

The activation energy for the hydrolysis of t-Butyl Chloride was found to be $76.188 \text{ kJ mol}^{-1}$, which is within 21.3% of the reference value. The pre-exponential factor in the arrhenius equation, A , was found to be $e^{21.336}$. The rate constant k was found to increase with increasing pump level.

Conversion level was found to change drastically after a change in reactor conditions, and then stabilize after 20 to 25 minutes. It was also seen that conversion level increased with decreasing pump flow rate.

References

- [1] *CSTR-study: The reaction of t-butyl chloride and water*, read 20th Oct. 2013. Available at http://www.nt.ntnu.no/users/preisig/Repository/TKP_4110_Felles_Lab/experiment%20descriptions/3-CSTR_study_hydrolysis_t-butyl_chloride_2013.pdf
- [2] Aylward, G. Findlay, T. *SI Chemical Data*, 6th ed.; John Wiley & Sons Ltd., 2008
- [3] Moelwyn-Hughes, E. A. Robertson R. E. Sugamori S. *The Hydrolysis of t-Butyl Chloride in Water: Temperature-dependence of the Energy of Activation*, 01. Jan 1965, downloaded 14th Sept. 2012, available at <http://pubs.rsc.org>, doi:10.1039/JR9650001965

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List of symbols

Symbol	Dimension	Description
A	s^{-1}	Constant in Arrhenius equation
C_i	mol L^{-1}	Concentration of component i
$(C_i)_f$	mole/L	Concentration of component i in the feed
$(C_i)_p$	mole/L	Concentration of component i in the product
C_{tBC}	mole/L	Concentration of tBC
C_{tBC_0}	mole/L	Start concentration of tBC
E_a	J mol^{-1}	Activation energy
k	s^{-1}	Rate constant
m	g	mass
M	g mol^{-1}	Molar mass
n	mol	moles
P	Dimensionless	System pump level
Q_f	mL min^{-1}	Calculated total volumetric flow of feed
r	$\text{mol mL}^{-1} \text{s}$	Reaction rate
R	$\text{J mol}^{-1} \text{K}$	Universal gas constant
T	$^{\circ}\text{C}$	Temperatur
T_{bath}	$^{\circ}\text{C}$	Temperatur of the water bath
$T_{reactor}$	$^{\circ}\text{C}$	Temperatur of the reactor
v_0	L s^{-1}	Volumetric flow at steady state
v_f	L s^{-1}	Volumetric flow of feed
v_p	L s^{-1}	Volumetric flow of products
V	mL	Reactor volume
X	no dimension	Conversion
τ	s	Mean bed-residence time

A Calculations

A.1 Amount of chemicals required

The concentration of the two feeds are given in the experimental section of the lab script.¹ Molar mass and density for tBC was found in SI Chemical data.² The values in table 8 were found by (A.1) and (A.2),

$$C = \frac{n}{V} \quad (\text{A.1})$$

$$m = Mn \quad (\text{A.2})$$

where C is the given concentration, V the total volume (1000 mL), n are moles, and M molar mass.

Table 8: Amounts of reactants and solvent needed

Compound	C [M]	V [mL]	m [g]
H ₂ O	35	630	630
tBC	0.025	2,77	2.315
MeOH	-	1370	-

The calculated values in table 8 is calculated as shown under: Calculations of feed 1 where the concentration of H_2O should be 35 M, which is equivalent to 35 mol of H_2O :

$$V_{H_2O} = \frac{35\text{mol} \cdot 18,016\text{g mol}^{-1}}{1\text{g mL}^{-1}} = 630\text{mL} \quad (\text{A.3})$$

where V_{H_2O} is the volume of water required in 1000 mL. The rest $1000\text{mL} - 630\text{mL} = 370\text{mL}$ is the amount of methanol needed.

In feed 2, the concentration of t-Butyl Chloride should be 0,025 M:

$$V_{tBC} = \frac{0,025\text{mol} \cdot 92,56\text{g mol}^{-1}}{0,84\text{g mL}^{-1}} = 2,76\text{mL} \quad (\text{A.4})$$

where V_{tBC} is the volume of t-Butyl Chloride needed to make 1000 mL of solution.

A.2 Constants

Data used for calculations can be found in Table 9

Table 9: The table shows variables and constants used for calculations. M , ρ and R were found from²

Variable	Value
V	207 mL
V_{tot}	2000 mL
m_{tBC}	2,33 g
M_{tBC}	92,57 g mol ⁻¹
R	8,314 JK ⁻¹ mol
ρ_{tBC}	0,84 g mL ⁻¹

A.3 Conversion level data

Table 10: Calculated conversion levels over time for all runs. The values are plotted in figure 6

Time [min]	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
	X	X	X	X	X	X
0	0,019	0,076	0,073	0,098	0,130	0,175
3	0,032	0,071	0,086	0,101	0,146	0,167
6	0,040	0,071	0,090	0,108	0,152	0,156
9	0,048	0,065	0,084	0,113	0,156	0,156
12	0,053	0,065	0,088	0,116	0,160	0,149
15	0,059	0,065	0,090	0,118	0,163	0,152
18	0,062	0,065	0,092	-	0,167	0,149
21	0,065	0,065	0,094	-	0,171	0,149
24	0,067	0,064	0,094	0,116	0,175	0,149
27	0,071	0,065	0,094	0,118	0,175	0,149
30	0,076	-	0,094	0,118	0,175	-
33	0,082	-	-	-	-	-
36	0,084	-	-	-	-	-
39	0,075	-	-	-	-	-
42	0,084	-	-	-	-	-

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Run 1 $T = 80^\circ\text{C}$, $P = 60$
 $t_{\text{inc}}(\text{min})$ pH

Therese Baché
Temperature ($^\circ\text{C}$)
 pH

Time	pH	$T(\text{pH-meter})$	$T(\text{Thermometer})$
0	3.02	29.5	29.1
3	3.05	29.5	29.1
6	3.05	29.5	29.1
9	3.09	29.5	29.1
12	3.09	29.5	29.1
15	3.09	29.5	29.1
18	3.09	29.5	29.1
21	3.09	29.5	29.1
24	3.10	29.5	29.1
27	3.09	29.5	29.1
Run 3	$T = 35^\circ\text{C}$, $P_{\text{water}} = 80$	$T_{\text{pH-meter}}$	$T_{\text{Thermometer}}$
0	3.04	33.3	33.0
3	2.97	33.6	33.3
6	2.95	33.7	33.4
9	2.98	33.7	33.4
12	2.96	33.7	33.4
15	2.95	33.7	33.4
18	2.94	33.7	33.4
21	2.93	33.7	33.4
24	2.93	33.7	33.4
27	2.93	33.8	33.4
30	2.93	33.8	33.4

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Run 2 $T = 30^\circ\text{C}$, $P = 80$

Run 4 , $T = 35^{\circ}\text{C}$, $P = 60$

Time	pH	$T(\text{pH-meter})$	$T(\text{thermo})$
0	2.91	33.9	33.6
3	2.90	34.0	33.6
6	2.87	34.0	33.6
9	2.85	34.0	33.7
12	2.84	34.0	33.7
15	2.83	34.0	33.7
18			
21			
24	2.84	34.0	33.7
27	2.83	34.1	33.7
30	2.83	34.1	33.7

Run 6 , $T = 40^{\circ}\text{C}$, $P = 80$

Time	pH	$T(\text{pH})$	$T(\text{thermometer})$
0		2.66	32.3
3		2.68	38.0
6		2.71	38.2
9		2.71	38.2
12		2.71	38.2
15		2.73	38.2
18		2.73	38.2
21		2.73	38.2
24		2.73	38.2
27		2.73	38.2
30		2.73	38.2

Run 5 $T = 40^{\circ}\text{C}$, $P = 60$

Time	pH	$T(\text{pH meter})$	$T(\text{thermometer})$
0	2.79	37.9	37.6
3	2.74	38.3	38.1
6	2.72	38.5	38.1
9	2.71	38.5	38.2
12	2.70	38.6	38.2
15	2.69	38.5	38.2
18	2.68	38.5	38.2
21	2.67	38.5	38.2
24	2.66	38.5	38.2
27	2.66	38.5	38.2
30	2.66	38.6	38.2

C Material Safety Data Sheets

D Risk Assessments