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

Øyvind Eraker, Kjetil Sonerud and Ove Øyås
Group B04

Supervisor: Miroslav Surma

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Abstract

The reaction of t-butyl chloride (tBC) and water was investigated in a CSTR reactor. While varying the temperature and residence time of the reactor, pH measurements were used to monitor the conversion level as a function of time. In all cases, the concentration of tBC in the feedstock and the molar feed ratio of water were held constant and the system was allowed to reach steady state conditions. Knowing that the rate-determining step of the reaction is the formation of the carbocation, an expression for the rate constant was derived from the mass balance of the system with the assumption of steady state conditions and zero accumulation. The conversion level, X, and the rate constant, k, was calculated each time steady state was reached.

From Arrhenius' equation, a linear expression was derived with the activation energy, E_a, as the slope. Plotting the natural logarithm of the rate constant, $\ln k$ as a function of temperature and applying linear regression, the activation energy was determined to 148,5 kJ/mol.

Contents

1   Introduction

In this laboratory exercise, the reaction of t-butyl chloride (tBC) and water in a CSTR reactor is investigated under various reaction conditions. Both reactants are diluted in methanol. The temperature and residence time of the reactor are varied, and pH measurements are used to monitor the level of conversion as a function of time. The concentration of tBC in the feedstock and the molar feed ratio of water are both held constant. In all cases, the system is monitored until the system can be assumed to have reached steady state conditions.

The forward rate constant of the hydrolysis of tBC is determined at all reaction conditions, assuming that the reaction is irreversible. The activation energy is also determined. The goal of the experiment is to achieve a fundamental understanding of the reaction kinetics by observing the changes induced by variations in temperature and residence time. This understanding may later be applied to large scale industrial processes involving similar reaction systems.

2   Theory

Formation of the carbocation is the rate-determining step in the hydrolysis of t-butyl chloride, as seen in Fig. 1.

The rate law of the reaction can then be expressed as

$$- r = kC_{tBC} \tag{2.1}$$

where $-r$ is the rate of disappearance of t-butyl chloride, k is the rate constant of the reaction and C_{tBC} is the concentration of t-butyl chloride. The reaction is carried out in a CSTR, as shown in Fig. 2. From the mass-balance of this system it is obvious that

$$\text{In - Out + Reacted = Accumulated} \tag{2.2}$$

Since this is a steady-state system with no accumulation, the equation takes the form

$$F_{tBC,0} - F_{tBC} = -rV \tag{2.3}$$

where $F_{tBC,0}$ is the rate of flow of t-butyl chloride into the reactor, F_{tBC} is the rate of flow of t-butyl chloride out of the reactor and V is the volume of the reactor. If the rate
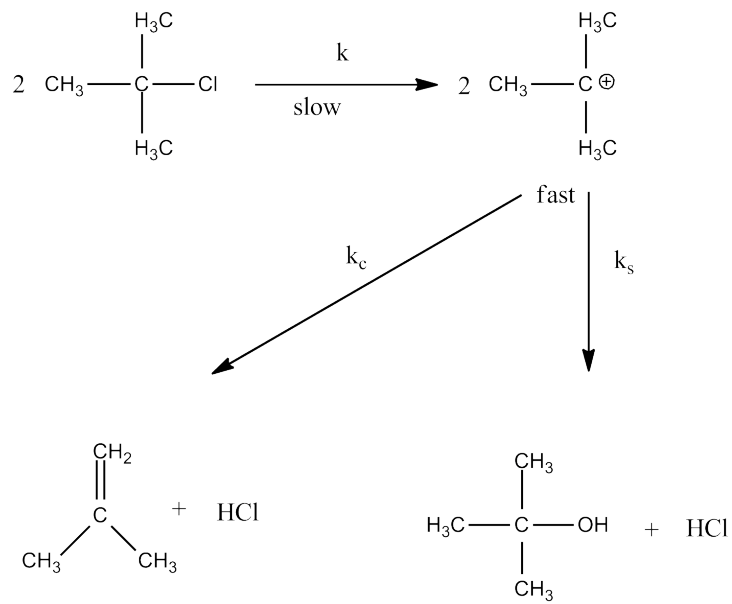
Figure 1: Reaction mechanism for the hydrolysis of t-butyl chloride. The formation of the carbocation in Step 1 is rate-determining. The subsequent parallell steps involving the formation of hydrochloric acid along with isobutylene and t-butanol respectively are both fast.
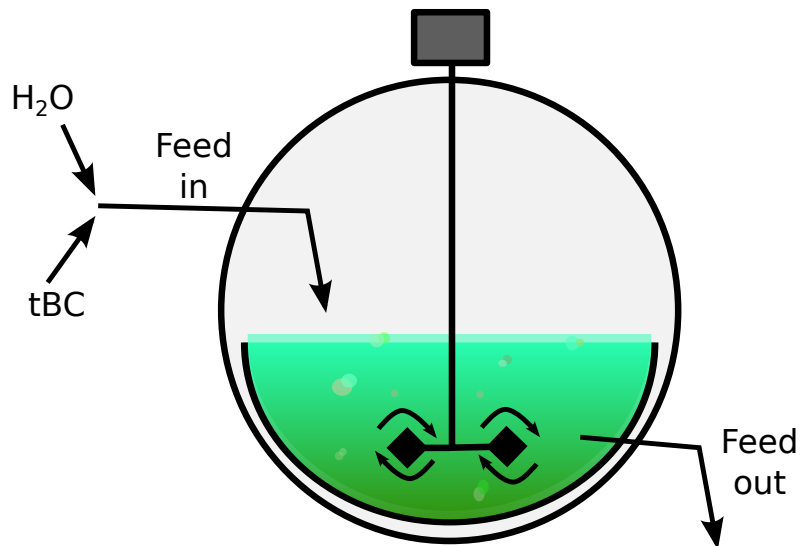

Figure 2: A flowchart showing the reaction system; the two inflows, the CSTR and the outflow from the reactor.

law from equation (2.1) is inserted into this equation, the expression takes the form

$$\frac{F_{tBC,0}}{V} - \frac{F_{tBC}}{V} = kC_{tBC} \tag{2.4}$$

The mean bed-residence time can be defined as

$$\tau = \frac{V}{Q_f} \tag{2.5}$$

where V is the reactor volume and Q_f is the total feed flow given by the calibration curve

$$Q_f = 0.0025P^2 + 0.0768P + 2.6752 \tag{2.6}$$

where P is the pump level and Q_f is measured in mL/min. Multiplying equation (2.4) with the mean bed-residence time, τ, yields

$$C_{tBC,0} - C_{tBC} = kC_{tBC}\tau \tag{2.7}$$

Solving for k gives

$$k = \frac{1}{\tau}\left(\frac{C_{tBC,0}}{C_{tBC}} - 1\right) \tag{2.8}$$

By measuring the concentration of H^+ (i.e. the pH), the concentration of t-butyl chloride in the flow out of the reactor will also have been determined. The stoichiometric ratio of t-butyl chloride to HCl is 1:1 (as can be seen in the reaction mechanism in Fig. 1), and it is therefore possible to determine the rate constant, k, as long as the reactor volume, V, is known.

The conversion level X is defined as

$$X_A = \frac{\text{Total moles of A reacted}}{\text{Moles of A fed to the reactor}} \tag{2.9}$$

For the hydrolysis of tBC, this can be written as

$$X = \frac{C_{tBC,0} - C_{tBC}}{C_{tBC,0}} = 1 - \frac{C_{tBC}}{C_{tBC,0}} \tag{2.10}$$

Determining the rate constant makes it possible to determine the activation energy, E_a, by use of a logarithmic Arrhenius plot. Arrhenius' equation is

$$k = Ae^{-E_a/RT} \tag{2.11}$$

where A is a constant preexponential factor, R is the universal gas constant and T is the temperature. Taking the logarithm of equation (2.11) gives

$$\ln k = \ln A - \frac{E_a}{RT} \tag{2.12}$$

By plotting $\ln k$ against $-\frac{1}{RT}$ in a linear plot and applying linear regression, E_a and $\ln A$ can be determined from the slope of the resulting curve and the intersection with the vertical axis respectively.

3 Experimental

3.1 Experimental setup

The experimental setup is shown and explained in Fig. 3.

3.2 Making the solutions

Feed 1

Feed 1 is supposed to contain 35 mol/L water in MetOH. 1000 mL of this is made by measuring out 35 moles of water, corresponding to $35 \text{ mol} \cdot 18.02 \text{ g/mol} = 630.7 \text{ g}$ water. This is then diluted with methanol to 1000 mL.

Feed 2

Feed 2 is supposed to contain 0.025 mol/L t-butyl chloride in MetOH. 1000 mL of this is made by measuring out 0.025 moles of t-butyl chloride, corresponding to $0.025 \text{ moles} \cdot 92.57 \text{ g/mol} = 2.3143 \text{ g}$ t-butyl chloride. This amount of t-butyl chloride should be weighed out in 100 mL methanol, and then be diluted to 1000 mL with methanol to minimize evaporation of t-butyl chloride.

3.3 Experimental procedure

The experimental procedure is repeated six times, with variations in temperature and pump level as shown in Table 1. The concentration of t-butyl chloride in the feed is the same throughout the experiment ($C_{tBC} = 0.025$ mol/L).
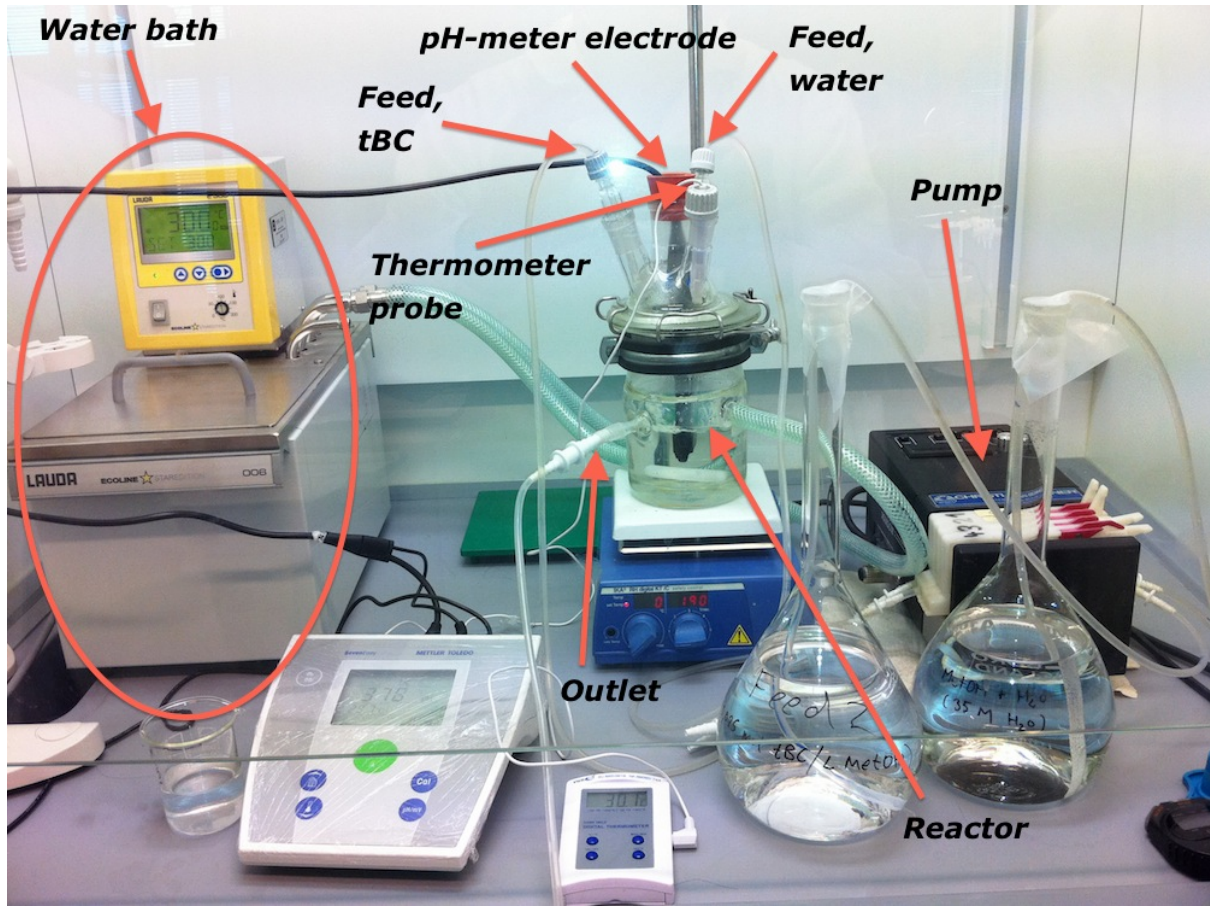
Figure 3: The experimental setup. The two feeds – one containing water, the other tBC – is added to the CSTR reactor through separate hoses and are driven from the storage bottles to the reactor by an adjustable pump. The reaction mixture is stirred by a magnetic stirrer. The temperature in the reactor is controlled by cycling water from a thermostatic water bath through the space between the inner compartment and outer walls. A thermometer and a pH meter are inserted through the top of the reactor and a stopwatch is used to measure the time between observations.

Table 1: Variations in the temperature of the water bath, T, and the pump level, P, throughout the experiment .

Run #	T [°C]	P [-]
1	30	60
2	30	80
3	35	60
4	35	80
5	40	60
6	40	80

First, the water bath temperature is set. The reactor is then filled with reactants in order to save time. The feed-hoses are connected to the reactant solutions and the clean pH-electrode, in/out-hoses and the product container are connected to the reactor. The stirring is turned on, and the pump is turned on and set to the required level. The pH value, temperature and elapsed time is noted every 3 minutes during the reaction, so that it is possible to know when the system approaches steady-state.

Between subsequent runs, it is only necessary to adjust the temperature and/or pump level, and note the same parameters as mentioned above. When all the experiments are done, the electrical equipment is shut off, the reactor emptied and the equipment cleaned.

4   Results

The results from the experiment are summarized in the tables 2 - 4 below.

Table 2: Variations in the pH of the reaction mixture with time, t. The temperature of the reactor was kept at $T = 30.1°C$ and the pump level, P, was kept at 60 for the first series and 80 for the second.

$P = 60$		$P = 80$	
t [min]	pH	t [min]	pH
0	≈ 7	0	≈ 3.3
6	≈ 5	3	≈ 3.4
9	≈ 5	6	≈ 3.15
12	≈ 4	9	≈ 3.10
15	≈ 3.8	12	≈ 3.0
17	3.65	15	3.00
18	3.60	16	3.00
19	3.55	-	-
22	3.45	-	-
24	3.40	-	-
25	3.35 †	-	-

The natural logarithm of the calculated rate constant, $\ln k$, was plotted against $-1/RT$ for both pump levels used in the experiment and two expressions for $\ln k$ as a function of temperature, T, were found by linear regression. The plot shown in Fig. 4 corresponds to

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† As the system had not reached the steady state when this value was recorded, the pH-value used for the calculations for $P = 60$ is the one found at steady state for $P = 80$. This means that pH $= 3.00$ was used.

Table 3: Variations in the pH of the reaction mixture with time, t. The temperature of the reactor was kept at $T = 34.3°C$ and the pump level, P, was kept at 60 for the first series and 80 for the second.

$P = 60$		$P = 80$	
t [min]	pH	t [min]	pH
0	≈ 3	0	2.62
3	≈ 2.9	2	2.62
5	2.82	5	2.62
8	2.74	8	2.62
10	2.71	10	2.62
11	2.70	12	2.62
12	2.69	-	-
13	2.67	-	-
14	2.66	-	-
15	2.65	-	-
16	2.64	-	-
17	2.63	-	-
18	2.62	-	-

Table 4: Variations in the pH of the reaction mixture with time, t. The temperature of the reactor was kept at $T = 38.8°C$ and the pump level, P, was kept at 60 for the first series and 80 for the second.

$P = 60$		$P = 80$	
t [min]	pH	t [min]	pH
0	≈ 2.6	0	≈ 2.4
2	2.52	2	2.42
4	2.53	4	2.42
6	2.51	6	2.43
8	2.48	8	2.43
10	2.46	10	2.43
12	2.45	12	2.43
14	2.44	14	2.41
16	2.43	17	2.41
17	2.42	18	2.40
18	2.42	19	2.41
19	2.41	-	-
20	2.41	-	-
21	2.41	-	-

pump level $P = 60$ and the one in Fig. 5 to $P = 80$. The values used in the construction of the plots are summarized in Table 5.

Table 5: Data for $\ln k$ and $-1/RT$ at the pump levels $P = 60$ and $P = 80$.

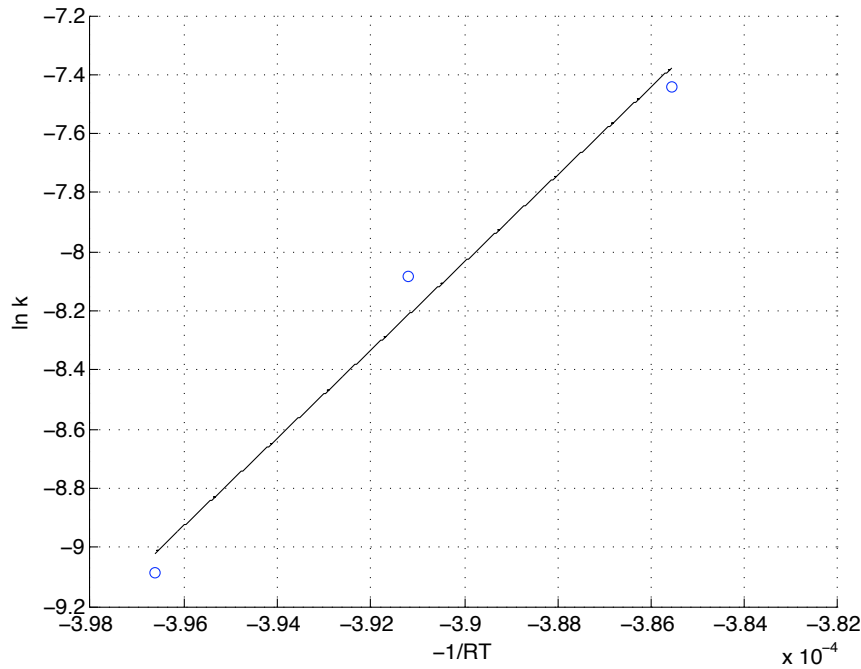|	$P = 60$		$P = 80$
$\ln k$ [-]	$-1/RT$ [mol/J]	$\ln k$ [-]	$-1/RT$ [mol/J]
-9.0866	$-3.966 \cdot 10^{-4}$	-8.665	$-3.966 \cdot 10^{-4}$
-8.082	$-3.911 \cdot 10^{-4}$	-7.661	$-3.911 \cdot 10^{-4}$
-7.441	$-3.855 \cdot 10^{-4}$	-7.019	$-3.855 \cdot 10^{-4}$

Figure 4: Plot of the natural logarithm of the rate constant, $\ln k$, against $-1/RT$ at pump level $P = 60$. A regression line is shown.

Linear regression gave the following expressions:

$$y = 148526x + 49.887, \ P = 60 \tag{4.1}$$

$$y = 148526x + 50.309, \ P = 80 \tag{4.2}$$

Here y corresponds to $\ln k$ and x to $-1/RT$. The activation energy, E_a is given by the slope of Eq. (4.1) and (4.2) and the natural logarithm of the preexponential factor $\ln A$ is given by the intersection. The results are given in Table **??**

The rate constant, k, the conversion level, X and the mean bed-residence time, τ, were

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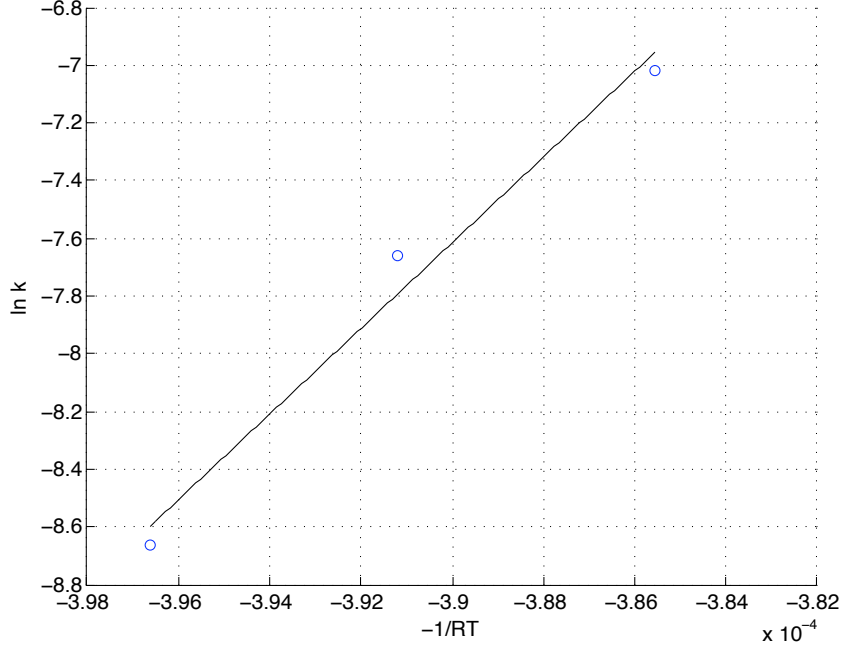
Figure 5: Plot of the natural logarithm of the rate constant, $\ln k$, against $-1/RT$ at pump level $P = 80$. A regression line is shown.

Table 6: The activation energy, E_a, and the natural logarithm of the preexponential factor, A, at the pump levels $P = 60$ and $P = 80$ found by linear regression.

P [-]	E_a [kJ/mol]	$\ln A$ [-]
60	148.526	49.887
80	148.526	50.309

calculated at steady state for all combinations of temperature and pump level. The results are summarized in Table 7.

Table 7: The activation energy, E_a, and the natural logarithm of the preexponential factor, A, at the pump levels $P = 60$ and $P = 80$ found by linear regression.

P [-]	τ [s]	T [°C]	k [s^{-1}]	X [-]
60	12.71	30.1	$1.13 \cdot 10^{-4}$	0.079
60	12.71	34.3	$3.09 \cdot 10^{-4}$	0.191
60	12.71	38.8	$5.87 \cdot 10^{-4}$	0.309
80	8.34	30.1	$1.72 \cdot 10^{-4}$	0.079
80	8.34	34.3	$4.71 \cdot 10^{-4}$	0.191
80	8.34	38.8	$8.94 \cdot 10^{-4}$	0.309

5 Discussion

It is observed that the pump level, P, does not affect the pH, and therefore not the conversion X. This can be seen from the definition of X, Eq. (2.10). As the initial concentration of tBC, $C_{tBC,0}$ is constant throughout the experiment, and the final concentration of tBC, C_{tBC}, is given by the pH, the conversion, X, will remain constant as long as the pH does so.

It is also observed that the conversion increases with increasing temperature, which is expected. The amount of tBC that reacts in the given mean bed-residence time will increase as the temperature increases because of the increase in reaction rate. The fact that the reaction rate increases with temperature follows from the fact that the reaction is assumed to follows Arrhenius kinetics, as in Eq. (2.11). The equation clearly shows that an increase in the temperature, T, leads to an increase in the rate constant, assuming that the activation energy, E_a, is positive.

As expected, the activation energy found from the experimental data with $P = 60$ and $P = 80$ is equal. The value of the activation energy stems from the chemical properties of the atoms that take part in the reaction, as well as the interactions between these and the solvent molecules. It is not affected by the flow rate, as this does not change any of these properties.

The experiment shows that the reaction rate, k, increases as the pump level, P, increases. This is in accordance with the theory for the experiment, as an increase in P is the same as a decrease in the mean bed-residence time, τ. As Eq. (2.8) shows, k is inversely proportional to τ. This can also be understood from a logic argument; if the conversion

is to remain constant, and the time the reactants have to react goes down (τ decreases), the value of the rate constant has to increase.

The activation energy is determined from the Arrhenius plots given in Fig. 4 and Fig. 5 using linear regression. As shown in Table 6, the result is $E_a = 148,5$ kJ/mol for both pump levels. This result does not seem to comply with the values found in the literature [3]. However, the experimental conditions in the cited experiment differ are not identical to the ones used in the current experiment, so the value should only be viewed as an indication. The reasons for the deviation, apart from the sources of error discussed below, are unknown.

There are several sources of error in this laboratory exercise. The volume of liquid in the reactor is not known accurately, but is approximated to be 207 mL. The reason for the uncertainty in the volume is caused by extensive stirring used to approach ideal mixing, which result in a conical shape of the liquid surface. Depending on the stirring speed, the volume may be either larger or smaller than the given value.

The pump seemed to pump the H_2O faster than the tBC, as there was about 50 mL more of the tBC-solution at the end of the experiment (the experiment lasted approximately 3 hours). This difference in flow of the two feed solutions will have caused the actual concentration of tBC to be lower than the theoretical value used in the calculations. This deviation will introduce an error that will propagate through all the results, leading to a decreased value for k and a consequently increased value for E_a.

Furthermore, the reactor is approximated as a CSTR, and ideal stirring is assumed. This will obviously introduce some degree of error, as the mixing in reality is not ideal. There might also be an error resulting from the fact that air bubbles in the hoses did cause the flow of the two reactants to be rather unsteady. Both these deviations may have affected the results.

The temperature readings might be inaccurate, as the three thermometers all showed different temperatures.

$$T_{wb} < T_{thermo} < T_{pH-meter} \tag{5.1}$$

where T_{wb} is the temperature of the water bath, T_{thermo} is the temperature of the thermometer in the reactor, and $T_{pH-meter}$ is the temperature reading from the pH-meter. It is assumed that T_{thermo} is the most accurate, and this is used in the calculations.

Trondheim, November 5, 2011.

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Øyvind Eraker   Kjetil Sonerud   Ove Øyås

6 References

[1] *CSTR study: The reaction of t-butyl chloride and water*, 2011. Viewed 3 November 2011. `http://www.nt.ntnu.no/users/preisig/Repository/TKP_4110_Felles_Lab/experiment%20descriptions/3_CSTR_study_hydrolysis_t-butyl_chloride_2010-08-20.pdf`.

[2] Fogler, S., 2006. *Elements of Chemical Reaction Engineering.* 4th ed. Pearson Education pp. 38-39

[3] Landgrebe, J.A., 1964. A simple kinetic investigation of an organic reaction mechanism. *Journal of Chemical Education*, Vol. 41 (10).

[4] Aylward, G. and Findlay, T., 2008. *SI Chemical Data.* 6th ed. John Wiley & Sons Australia.

A   Calculations

Data used in the calculations are given in Table 8.

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Table 8: Data used in calculations.

Variable	Value
$V^{[1]}$	207 mL
V_{tot}	2000 mL
R [4]	8.3145 J/K mol
m_{tBC}	2.33 g
M_{tBC}[4]	92.57 g/mol

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The concentration of t-butyl chloride (tBC) in the feed, $C_{tBC,0}$, was calculated from the expression

$$C_{tBC,0} = \frac{m_{tBC}}{M_{tBC}V_{tot}} \tag{A.1}$$

where m_{tBC} is the mass of the weighed out tBC, M_{tBC} the molar mass of tBC and V_{tot} the total volume of the two feed solutions.

The concentration of H^+, C_{H+}, was calculated from the measured pH using the expression

$$C_{H^+} = 10^{-\text{pH}} \tag{A.2}$$

and the concentration of tBC, C_{tBC}, at the corresponding point in the experiment was found from the mass balance of he system:

$$C_{tBC} = C_{tBC,0} - C_{H^+} \tag{A.3}$$

The total feed flow Q_f was calculated using Eq. (2.6) and the mean bed-residence time, τ, from Eq. (2.5). From this, the rate constant, k, was found using Eq. (2.8).

The conversion level, X, was found using Eq (2.10).

Kjemikaliekort

	STOFFNAVN *2-chloro-2-methylpropane (t-butyl chloride)*			FORMEL C_4H_9Cl	
					HELSEFARE *Avoid inhalation or ingestion.*
FYSIKALSKE DATA	M_m	fl.p.	Ekspl.gr.	BRANNFARE *Highly flammable liquid and vapour.*	
	92,57 g/mol	-	-	REAKSJONSFARE	
VERNETILTAK	*Avoid contact with skin and eyes, Avoid inhalation of vapour or mist. Use safety goggles and rubber/plastic gloves. Be sure to work under a fume hood.*			ADMINISTRATIV NORM	
HELSEFARE Innånding Svelging Hud Øyne	Inhalation may cause burning of the nose and throat. Can cause nausea and dizziness. Risk of aspiration with chemical pneumonia. Burning in mouth and throat. Nausea and vomiting can occur. Aspiration into the lungs during vomiting or ingestion can cause chemical pneumonia. Can cause unconsciousness in severe cases. Systemic effects: Risk of kidney and liver damage. May cause cardiovascular effects. Slightly irritating. Burning. May cause defatting and cause redness and cracking. Irritating to eyes. May cause burning and watering eyes.			BRANNSLUKKING *For small (incipient) fires, use media such as "alcohol" foam, dry chemical, or carbon dioxide. For large fires, apply water from as far as possible. Use very large quantities (flooding) of water applied as a mist or spray; solid streams of water may be ineffective. Cool all affected containers with flooding quantities of water.* MERKNADER	
FØRSTEHJELP	ØYNE *Flush eyes with water as a precaution.* HUD *Wash off with soap and plenty of water. Consult a physician.*		SVELGING *Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.* INNÅNDING *If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.*		

SPESIELLE MERKNADER	
SPILL/ RESTER	*Contain spillage, and then collect with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and place in container for disposal according to local /national regulations.* *Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all sources of ignition.*
LAGRING	*Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.*

Kjemikaliekort

	STOFFNAVN *Methanol*			FORMEL CH_3OH	
					HELSEFARE *Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.*
FYSIKALSKE DATA	M_m	fl.p.	Ekspl.gr.	BRANNFARE *Highly flammable.*	
	32,04 g/mol	-	-	REAKSJONSFARE	
VERNETILTAK	*Avoid contact with skin and eyes. Avoid inhalation of vapour or mist. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.Use safety goggles and rubber/plastic gloves. Be sure to work under a fume hood.*			ADMINISTRATIV NORM	
HELSEFARE Innånding Svelging Hud Øyne	*In general, methanol is toxic.* Toxic if inhaled. Toxic if swallowed. Can cause damage to organs. May cause blindness or (in the worst case) death. Toxic in contact with skin. Irritating. may cause serious eye damage.			BRANNSLUKKING *Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.* MERKNADER	
FØRSTEHJELP	**ØYNE** *Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.* **HUD** *Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.*		**SVELGING** *Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.* **INNÅNDING** *If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.*		

SPESIELLE MERKNADER	
SPILL/ RESTER	*Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations. Avoid breathing vapors, mist or gas. Ensure adequate ventilation.* *Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable.*
LAGRING	*Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.*

Hydrolysis of t-butyl chloride

$W_{H_2O} = 630,71$ g

→ diluted to 1000 mL with MeOH.

100 mL MeOH + 2,33 g t-butyl chloride

→ diluted to 1000 mL with MeOH

#	pH	T	P
0	~ 7	30	60
6	~ 5		
9	~ 5		
12	~ 4		
15	~ 3,8		
17	3, 65		
18	3, 60		
19	3, 55		
22 ~~A~~	3, 45		
24	3, 40		
25	3, 35	30,1	steady-state ?

(probably not quite...)

#	pH	T	P
0	~ 3, 3	30	80
3	~ 3, 4		
6	~ 3,15		
9	~ 3, 10		
12	~ 3, 0		
15	3, 00		
16	3, 00	30,1	

#	pH	T	P
0	~3	35	60
3	~2,9		
5	2,82		
8:15	2,74		
10	2,71		
11 ~~#~~	2,70		
12	2,69		
13	2,67		
14	2,66		
15	2,65		
16	2,64		
17	2,63		
18	2,62	34,3	

Temperaturen økte noe gjennom serien.

#	pH	T	P
0	2,62	35	80
2	2,62		
5	2,62		
8	2,62		
10	2,62		
12	2,62	34,3	

#	pH	T	P
0	~2,6	40	60
2	2,52		
4	2,53		
6	2,51		
8	2,48		
10	2,46		
12	2,45		
14	2,44		
16	2,43		
17	2,42		
18	2,42		
19	2,41		
20	2,41		
21	2,41	38,8	

#	pH.	T	P
0	~2,40	40	80
2	2,42		
4	2,42		
6	2,43		
8	2,43		
10	2,43		
12	2,43		
14	2,41		
187	2,41		
18	2,40		
19	2,41	38,8	

(no more H_2O)