Kinetic study of ethyl iodide and NaOH in a batch reactor

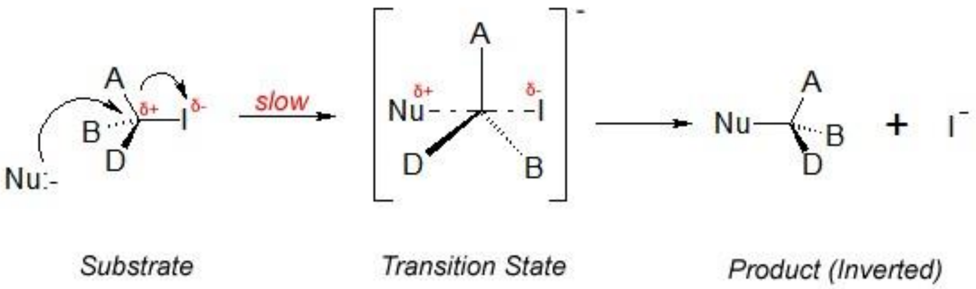
The reaction between ethyl iodide (C_2H_5I) and NaOH shall be studied at different reaction conditions in a batch reactor. The experiment will be performed under N_2 atmosphere, since ethyl iodide reacts with O_2. The progress of the reaction is recorded by monitoring the consumption of NaOH. The solvent consists of water and dimethyl sulfoxide (DMSO).

The task of the exercise is to study the influence of three different parameters, temperature, reactant concentration and composition of the solvent, on the reaction rate. Each group will investigate one of these parameters with two others fixed.

The rate constant of the reaction shall be determined, assuming irreversible reaction. Activation energy shall be calculated when the influence of temperature is studied.

1. Theory

The reaction between ethyl iodide and NaOH is a typical bimolecular nucleophilic substitution reaction. Nucleophilic substitution is the reaction between an electron pair donor (the nucleophile, Nu) and an electron pair acceptor (the electrophile).



The reaction rate depends on the nature of both nucleophile and the leaving group in the substrate, in this case is I^-. The reaction rate also depends on the solvent. Polar solvent can enhance the reactivity of the nucleophile and promote the reaction.

2. Kinetics

For a constant-volume batch reactor, the reaction rate, r_A, can be expressed as (H. Scott Fogler chapter 1.3, 2.2):

$$\frac{dC_A}{dt} = r_A \qquad (1)$$

Where C_A is the concentration of reactant A, t is the time, and r_A is the reaction rate.

The dependence of the reaction rate on the concentrations of the reactants, using the power law model, can be expressed as (H. Scott Fogler chapter 3.2):

$$-r_A = k_A C_A^{\alpha} C_B^{\beta} \qquad (2)$$

Where r_A is the reaction rate, k_A *is the reaction rate constant,* C_A and C_B are the concentrations of reactant A and B, and *α* and *β* are their respective stoichiometric factor. The reaction order, *n*, is then given as:

$$n = \alpha + \beta \qquad (3)$$

Combining equation (1) and (2), and using integral method, the reaction rate constant can be determined. For the reaction between C_2H_5I and NaOH, it occurs on a 1:1 molar ratio, and we always add C_2H_5I and NaOH to the reactor in a 1:1 molar ratio. What are the rate expressions for first- and second-order reaction? Which reaction order do you think it is for this reaction?

The temperature influence on the reaction rate constant can be described by Arrhenius equation (H. Scott Fogler chapter 3.3):

$$k_A = Ae^{-E/RT} \qquad (4)$$

Where k_A reaction rate constant
A preexponential factor
E activation energy, J/mol
R gas constant, 8.314 J/mol·K
T absolute temperature, K

3. Experimental

Reaction conditions

The reaction conditions are shown in Table 1.

Table 1. Reaction conditions for reaction temperature, initial concentration and mole fraction of DMSO in solvent.

Reaction parameters	Lower limit	Moderate limit	Upper limit
Temperature, T, [°C]			
Initial reactant concentration, $C(OH^-)$, [mol/L]			
Mole fraction of DMSO, X_{DMSO}			

V_{tot} =350ml. The specific conditions will be given later to each group.

For example, if the temperature effect is studied, you might be asked to perform 3 experiments at 35, 45 and 55°C respectively, while having fixed $C(OH^-)$=0.06 mol/L and X_{DMSO}=0.5 .

Reagents

NaOH	1 M	Solution
HCl	0.01 M	Solution
DMSO		Liquid
Ethyl iodide		Liquid

Please find the molecular weight and specific gravity (density) in Chemical data sheet (MSDS) for calculation. MSDS for all chemicals can be found above the chemical cabinet in felleslab room in Norwegian and Englsh.

Procedure

1. Measure the amounts of DMSO, distilled water, and NaOH solution, and premix them in a suitable container inside a fume hood. For those who are going to vary temperature, it is advisable to make one huge batch that will last for all three experiments; for those who vary reactant concentration or DMSO mole fraction, you have to make a new solution for each experiment.
2. Open the batch reactor and add premixed solution of DMSO, water, and NaOH to the reactor. **NEVER** add NaOH through an open neck in the reactor lid!!! NaOH is good glue for glass and you will never be able to remove the glass plug again if you spill even one drop of NaOH there!
3. Reconstruct the reactor with the lid, thermometer, N_2 gas connection and stirring. Start N_2 flow, and heat the water bath.
4. Wait the temperature to stabilize to desired temperature. That is very important! Otherwise, you may get really bad data.
5. While waiting for the temperature, you can prepare all of the Erlenmeyer flasks with approximately 75ml of distilled water and 4-5 droplets of phenolphthalein, and put the flasks on the ice bath, ready for samples. The reaction more or less stops when you add your samples to the cold solution. This is also the most accurate definition about when the samples are taken.
6. While waiting, you can also take the first sample (5ml) from the reactor (only NaOH and solvents) and do this baseline titration. Then you know approximately how much HCl you have to add for the titration of samples later on.
7. Prepare the stop watch and make sure it is in order. Then ethyl iodide can be added to the reactor through an open neck and the stop watch is started. Because of the high density of ethyl iodide, it may drip at a moderate pace when you use an automatic pipette to measure and to transfer ethyl iodide to the reactor. So the C_2H_5I bottle should be held as close as possible to the open neck of the reactor. It can be a little difficult to manage this without spilling, but it is possible. If you spill one or two drops, it may introduce some inaccuracy but it won't change the overall trend with the experiment.
8. Remove samples with varying intervals, frequent in the beginning (irreversible area) and with increasing intervals towards the end (the reaction gradually becomes reversible). Total reaction time depends on the reaction conditions. Remove enough samples to get a good regression line in the irreversible area.
9. Titrate the samples against 0.01 M HCl until a color change is observed (you can use magnetic stirring). The amount of reacted NaOH can then be calculated and used to find the reaction rate constant.
10. Clean the reactor and flasks and start your next experiment (step 2).
11. When the experiment is over, clean everything and leave the lab as clean as you found it!

Exercise: (Things you MUST do)

Before the Lab: (to be approved by supervisor before you get access to the lab. Not done=no lab)

1. Read and learn the apparatus card and MSDS about the chemicals used in the experiment (especially on hazards and safety). The apparatus card was put up on the wall of the fume hood where the experiment is.

2. Calculate amounts of reactants and solvents for the given reaction conditions.

3. Look at the reaction mechanism. Try to understand what is happening.

4. Prepare a work plan that should include:
    - theoretical introduction
    - calculated amounts of all the reactants
    - a scheme of the experiment setup
    - how the experiments will be organized
    - main risks regarding the procedure AND the use of chemicals
    - waste handling

After the Lab: (to be included in the report)

1. Calculate the reaction rate constant.

2. Calculate the activation energy (Only for groups who investigate the influence of temperature).

3. Discuss the effect of different parameters (temperature, reactant concentration and compositions of the solvent) on the reaction rate.

4. Give the rate expression for zero-, first- and second-order reaction. Which reaction order is it for this reaction?

5. Discuss the results (including the uncertainties during the experiment) and draw conclusions.

6. Include a copy of the log you kept with your data.