



Organic Chemistry I Nucleophilic Substitution Reactions of Alkyl Halides Lab

Organic Chemistry I (Camden County College)

Lab 8 - Nucleophilic Substitution Reactions of Alkyl Halides

Part I - Purpose:

The purpose of the experiment is to understand how the structure and leaving group of an alkyl halide, the effect and concentration of a nucleophile, and the polarity of a solvent take an effect when carrying out S_N1 and S_N2 mechanisms.

Part II - Results:

Observations

Group 1:

Alkyl Halide	Part 1	Part 2
1 – bromobutane	5 seconds	2 minutes
2 – bromobutane	10 - 11 minutes	1 minute
2 – bromo – 2 – methylpropane	3 minutes	Immediate
Bromobenzene	8 minutes	No reaction

Group 2:

Alkyl Halide	Part 1	Part 2
1 – chlorobutane	1 second	10 seconds
2 – chloro – 2 – methylpropane	No reaction	Immediate
1 – chloro – 2 – butene	1 second	10 seconds

Group 3:

Alkyl Halide	Part 1	Part 2
1 – bromobutane	30 seconds	5 seconds
2 - bromobutane	11 minutes	5 seconds
1 – chlorobutane	7 minutes	6 minutes
2 – chlorobutane	No reaction	5 minutes

Alkyl Halide	Part 3
2 – chlorobutane in 1% Ethanolic Silver Nitrate Solution	5 minutes (without heat)
2 – chlorobutane in 1% Silver Nitrate in a mixture of 50% Ethanol and 50% Water	10 seconds

Data

Substances Used:

Substance:	Amount:
18% Solution of Sodium Iodide in Acetone	1 mL
1% Ethanolic Silver Nitrate Solution	1 mL
1% Silver Nitrate in a mixture of 50% Ethanol and 50% Water	1 mL
Ethanol	1 mL

Alkyl Halides:

Substance:	Amount:
1 – chlorobutane	0.1 mL
1 – bromobutane	0.1 mL
2 – chlorobutane	0.1 mL
2 – chloro – 2 – methylpropane	0.1 mL
Bromobenzene	0.1 mL
1 – chloro – 2 – butene	0.1 mL
1 – chloro – 2 – methylpropane	0.1 mL
2 – bromobutane	0.1 mL
2 - bromobutane	0.1 mL

Part III - Discussion/Conclusion:

Discussion

The formation of a precipitate indicates that a reaction took place:

The first part of the experiment with sodium iodide in acetone should have a precipitate form for the halides that favor S_N2 reactions. Sodium Iodide in Acetone has a low polarity, thus will favor S_N2 reactions and react with halides with the appropriate structure. Halides with a primary structure should react the quickest. Because the S_N2 reaction is a one-step mechanism, a carbocation rearrangement does not take place, thus a less sterically hindered structure is preferred for the nucleophile to attack and cause the loss of the leaving group. Halides with a secondary structure would require more time to react. During the experiment, an increase in temperature may be necessary, for it speeds up the rate of reaction. Furthermore, vinylic and aryl halides will not react due to the double bonds repelling the nucleophile; halides with a tertiary structure will not react due to the inability for the nucleophile to attack the carbon.

The second part of the experiment with an ethanolic silver nitrate solution should have a precipitate form for the halides that favor S_N1 reactions. Silver nitrate solution has a high polarity, thus will favor S_N1 reactions and react with halides with the appropriate structure. Halides with a tertiary structure should react the quickest. Because the S_N1 reaction is a two-step mechanism, a carbocation rearrangement takes place following the loss of the leaving group, thus a more sterically hindered structure is preferred so that the most stable carbocation is formed before the nucleophilic attack. Halides with a secondary structure would require more time to react. During the experiment, an increase in temperature may be necessary, for it speeds up the rate of reaction. Furthermore, vinylic and aryl halides will not react due to the difficulty involved when forming the carbocation intermediate; halides with a primary structure will not react due to the inability to form a stable carbocation.

The third part of the experiment with 2-chlorobutane with one percent silver nitrate in a 1:1 mixture of ethanol and water should have a precipitate form. Because silver nitrate in ethanol and water is still polar, though diluted, the reaction will favor S_N1 when combined with the halide; however, because 2-chlorobutane has a secondary structure, the reaction will not take place immediately. When compared to the theoretical results of 2-chlorobutane in an ethanolic silver nitrate solution, the reaction should take longer, for the solvent is less effective as a protic solvent. A less effective polar protic solvent has less hydrogen ions able to be donated, thus takes longer or requires the addition of heat to break additional bonds.

Theoretical Results

Part 1 and 2:

Group 1:

Alkyl Halide	Part 1 (Sodium Iodide in Acetone):	Part 2 (Ethanolic Silver Nitrate Solution):
1 – bromobutane	Immediate	No reaction
2 – bromobutane	After a few minutes	After a few minutes
2 – bromo – 2 – methylpropane	No reaction	Immediate
Bromobenzene	No reaction	No reaction

Group 2:

Alkyl Halide	Part 1 (Sodium Iodide in Acetone):	Part 2 (Ethanolic Silver Nitrate Solution):
1 – chlorobutane	Immediate	No reaction
2 – chloro – 2 – methylpropane	No reaction	Immediate
1 – chloro – 2 – butene	No reaction	No reaction

Group 3:

Alkyl Halide	Part 1 (Sodium Iodide in Acetone):	Part 2 (Ethanolic Silver Nitrate Solution):
1 – bromobutane	Immediate	No reaction
2 – bromobutane	After a few minutes	After a few minutes

1 – chlorobutane	Immediate	No reaction
2 – chlorobutane	After a few minutes	After a few minutes

Part 3:

Alkyl Halide	
2 – chlorobutane in 1% Ethanolic Silver Nitrate Solution	After a few minutes
2 – chlorobutane in 1% Silver Nitrate in a mixture of 50% Ethanol and 50% Water	After a few minutes

Inconsistencies when comparing experimental and theoretical results:

Group 1

- Part 1 (Sodium Iodide in Acetone):
 - 2-bromo-2-methylpropane should have not reacted due to its tertiary structure
 - Bromobenzene should have not reacted due to it being an aryl halide
- Part 2 (Ethanolic Silver Nitrate Solution):
 - 1 – bromobutane should have not reacted due to its primary structure

Group 2

- Part 1 (Sodium Iodide in Acetone):
 - 1-chloro-2-butene should have not reacted due to it being a vinylic halide
- Part 2 (Ethanolic Silver Nitrate Solution):
 - 1 – chlorobutane should have not reacted due to its primary structure
 - 1-chloro-2-butene should have not reacted due to it being a vinylic halide

Group 3

- Part 1 (Sodium Iodide in Acetone):
 - 1 – chlorobutane should have reacted immediately due to its primary structure
 - 2 – chlorobutane should have reacted after a few minutes with the addition of heat due to its secondary structure
- Part 2 (Ethanolic Silver Nitrate Solution):
 - 1 – bromobutane should have not reacted due to its primary structure
 - 1 – chlorobutane should have not reacted due to its primary structure

Part 3

2 – chlorobutane in 1% Silver Nitrate in a mixture of 50% Ethanol and 50% Water should have taken longer to form a precipitate without the addition of heat when compared to 2 – chlorobutane in 1% Ethanolic Silver Nitrate Solution since the water creates a less effective polar protic solvent.

Conclusion

The data gathered produced a lot of inconsistencies between the experimental and theoretical results. There are several causes for error when carrying out this procedure: (1) inaccurate record of time; (2)

incorrect observations of the formation of precipitate; or (3) the reaction tubes were not completely clean/dry:

1. It is crucial for this experiment that an accurate record of time is kept. Time is used to observe the rate of reaction in the formation of a precipitate. Although not all reactions will take place, it is important that the time is properly recorded for those that do so that it can be better understood how different aspects (i.e., structures of a halide, polarity of the solvent, and temperature) affect the overall reaction. For example, it is expected that both reactions in part three take a few minutes to occur; however, if the time was not precisely recorded, it is impossible to compare the relationship between the halide and solvent.
2. A precipitate is a solid formed as the product of a chemical reaction. Throughout the experiment, the formation of a precipitate is the indicator that a specific mechanism took place, whether it be S_N1 or S_N2 . Although it is quite clear what mechanism caused the precipitate formation based on the characteristics of the halide and solvent, whether or not an actual precipitate formed can be misconstrued. At several instances throughout the experiment, there was uncertainty in whether or not there was a precipitate or just discoloration. Because this observation is an ultimatum for deciding whether or not a reaction occurred, misinterpretation will have dire effects on the data.
3. Expanding on the prior source of error involving the formation of a precipitate: if there was residue or traces of water in the reaction tube when carrying out the procedure, such contamination can have a huge effect on the data. Whether the contamination has a chemical effect on the reaction, or just alters the appearance of the mixture, it would cause for a false representation for the specific mechanism being observed.

Questions:

1. What would be the effect of carrying out the sodium iodide in acetone reaction with the alkyl halides using an iodide sodium half as concentrated?

If the iodine solution is half as concentrated, then the reaction would take place at half of the rate producing only half of the amount of precipitate.

2. The addition of sodium or potassium iodide catalyzes many S_N2 reactions of alkyl chlorides of bromides. Explain.

The positive charge of the sodium or potassium will assist in the loss of the leaving group making it easier for the nucleophilic attack. In addition, the iodide is weak enough so that it doesn't react in the solution.

3. In S_N1 reactions, the intermediate carbocations can eliminate a proton to yield alkenes or react with the solvent to yield ethers. Draw the structures of the byproducts of this type that would be derived from the reaction of the carbocations derived from 2-bromo-2-methylbutane in ethanol.

Work Cited:

Williamson, Kenneth L., and Katherine M. Masters. "Chapter 17 – Nucleophilic Substitution Reactions of Alkyl Halides". *Macroscale and Microscale Organic Experiments*. 6th ed. Mason, Ohio: Cengage Learning, 2011. 196 - 203. Print.