

Relative reactivity of alkyl halides



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Introduction

Nucleophilic substitution of alkyl halides can proceed by two different mechanisms - SN2 and SN1. The purpose of the experiment was to identify the effects that the alkyl group and the halide-leaving group have on the rates of SN1 reactions, and the effect that the solvent has on the rates of SN1 and SN2 reactions. The SN1 mechanism is a two-step nucleophilic substitution or unimolecular displacement. In the first step of the mechanism, the carbon-halogen bond breaks, and the halide ion leaving group leaves in a slow, rate-determining step to form a carbocation intermediate. The carbocation intermediate is then immediately detained by the weak nucleophile in a fast, second step to give the product. A solution of ethanol with some silver nitrate may be added provided the weak nucleophile - the alcohol. If an SN1 reaction occurs, the alkyl halide will dissociate to form a carbocation, which will then react with the ethanol to form an ether. Since there is not a strong nucleophile present, the cleavage of the carbon-halogen bond is encouraged by the formation and precipitation of silver bromide.

The halide ion will combine with a silver ion from the silver nitrate to form a silver halide precipitate, which will advise that a reaction has occurred.

+ AgBr + NO₃⁻

Figure 1: The SN1 mechanism of 2-Bromo-2-methylpropane and silver nitrate. The nucleophile would have been ethanol while the silver nitrate would have disassociated to form a silver halide precipitate. The more stable

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the carbocation, the quicker the reaction. Therefore, SN1 reactions desire tertiary substrates most, followed by secondary, and lastly primary. Because the strength of the nucleophile is unimportant, an ionizing solvent is needed. Water is the best solvent, followed by methanol, ethanol, propanol, and lastly acetone. In experiment two, the tertiary 2-Bromo-2-methylpropane was the most favored reactant followed by the secondary 2-bromobutane, the primary 1-bromobutane, and the primary 1-chlorobutanol. This order is determined by whether the molecule is primary, secondary, or tertiary. 2-bromo-2-methyl propane + AgNO₃ + (CH₃)₂CO AgBr + ethyl-t-butyl ether + isobutylene.

Figure 2: The SN2 mechanism of 2-Bromo-2-methyl propane with AgNO₃ in (CH₃)₂CO. The SN2 reaction mechanism is a one-step, bimolecular displacement in which the bond-breaking and bond-making processes occur simultaneously. The SN2 reaction requires a strong nucleophile. The order of reactivity is the opposite of the SN1 reaction because the nucleophile must attack from the back, and is favored with the least steric hindrance. The halide attached to a primary carbon is easier to attack from the back. In experiment one, the 1-chloroquine was the most favored reactant followed by the primary 1-bromobutane, the secondary 2-bromobutane, and the tertiary 2-Bromo-2-methylpropane. This order is determined by whether the molecule is primary, secondary, or tertiary. " SN2 reactions are particularly sensitive to steric factors since they are greatly retarded by steric hindrance (crowding) at the site of reaction. In general, the order of reactivity of alkyl halides in SN2 reactions is methyl > 1° > 2°. The 3° alkyl halides are so crowded that they do not generally react by an SN2 mechanism. " 1 1-

chloroquine and NaI-acetone -----> 1-iodobutane + NaCl (precipitate) In general, weaker bases make better-leaving groups.

SN1 and SN2 reactions show the same trends, but SN1 is more sensitive. The reactants favored in the SN2 mechanism are the opposite of the SN1 reaction. the primary 1-chloroquine was most favored, followed by the primary 1-bromobutane, the secondary 2-bromobutane, and tertiary 2-Bromo-2-methylpropane. Reagents with molecular weight, density, melting point, and boiling point. Five drops of each of the following reagents were added to the test tubes in numerical order: 2-Bromo-2-methylpropane, 2-bromobutane, 1-bromobutane, 1-chloroquine. Twenty drops of NaI in acetone were added to each test tube, the time of the first drop was recorded, and the tubes were mixed. The exact time of the first sign of cloudiness in each test tube was noted. The exact time of the first sign of precipitation was noted. If no reaction occurred within five minutes, the test tube was placed in a warm water bath. No color change was observed, only a change in the cloudiness of the solutions. For part B, the test tubes were rinsed with ethanol and then the same amount of each alkyl halide was placed into each test tube. Twenty drops of silver nitrate in ethanol was added to each of the four test tubes, and the exact time that the first drop was added to each test tube was noted. The exact time of the first sign of cloudiness in each test tube was noted. The exact time of the first sign of precipitation was noted.

If no reaction occurred within five minutes, the test tube was placed in a warm water bath. No color change was observed, only a change in the cloudiness of the solutions. For part C, four clean test tubes were acquired and numbered 1-4. 1 mL of 1: 1 methanol and water was added to the first

test-tube; 1mL of 1: 1 mixture of ethanol/water was added to the second test tube; 1mL of 1: 1 mixture of 1-propanol/water was added the third test tube, and 1 mL of 1: 1 mixture of acetone/water was added to the fourth test tube. Three drops of . 5M NaOH and three drops of 1% phenolphthalein were added to each test tube. Three drops of 2-Bromo-2-methylpropane were added to each test tube, and the exact time that the first drop was added to each tube was noted. The tubes were swirled, and the disappearance of the pink color was observed. The final color of each solution was yellow. The primary 1-bromobutane completed first, followed by the primary 1-chloroquine. The secondary 2-bromobutane completed third, and the tertiary 2-Bromo-2-methylpropane finished last. The 1-bromobutane finished before the 1-chloroquine because bromine was a better leaving group than chlorine. This is because bromine is bigger and less electronegative than chlorine. Therefore the bromine did not form as tight of bonds with carbon as chlorine, and could more easily leave the group. In experiment B, the results followed the trend hypothesized for SN2 reactions in the introduction.

The tertiary finished first, followed by secondary, followed by the primaries. 1-bromo-2-methylpropane finished first because of its tertiary nature. The secondary 2-bromobutane finished second. The primary 1-bromobutane finished third, followed by primary 1-chloroquine. The rate-limiting formation of the carbocation decided this pattern. The 1-bromobutane finished before the 1-chloroquine because bromine was a better leaving group than chlorine. In experiment C, the results did not follow the trend hypothesized for the solvent effects on the SN1 reaction. Methanol should have finished first, then ethanol, then propanol, and lastly acetone. The results were the exact

opposite; acetone finished first, then propanol, then ethanol, and lastly methanol. The boiling points of the solutions were responsible for this result. The bottles containing the solutions must have been left open for a prolonged period of time before use to allow evaporation. The acetone, propanol, and ethanol must have been mainly water, and thus finished earlier than methanol. The first error pertained to experiment C. The results were backward and had to have been due to the boiling points of the solutions. The solutions that evaporated the most before the experiment finished quickest because of the ratio of water to the specific solution. The error could have been corrected by remaking the solutions before the lab. The second error pertained to experiment B. The experiment was performed twice because the test tubes were not washed with ethanol between uses. The use of water to wash the test tubes sped up the reactions because the water was the best solvent for the SN1 reactions. The use of ethanol to wash the test tubes had little effect on the rate of the reactions because it was the third-best solvent after water and methanol.

Conclusion

The purpose of the experiment was to identify the effects that the alkyl group and the halide leaving group had on the rates of SN1 and SN2 reactions, and the effect that the solvent had on the rates of an SN1 reaction. The purpose was achieved because the tertiary alkyl group sped up the SN1 reaction most, while the primary alkyl group sped up the SN2 reaction most. The effect of the halide-leaving group was established because bromine was bigger and less electronegative than chlorine, which allowed bromine to leave the group sooner than chlorine due to the less

strong bonds of bromine. The solvents' effect on the rates of the SN1 reaction was due to the encouragement of the cleavage of the carbon-halogen bond, instead of the use of a strong nucleophile. An improvement for the experiment would have been to mix the solvents just before lab to reduce the amount of solvent that boiled off at room temperature. More accurate measurements such as 1 mL measured in the graduated cylinder would have been more precise and consistent than the addition of a specific number of drops.

Reference

1. The SN2 Reaction. University of Texas Educational Website. 11 September 2012.
2. <http://iverson.cm.utexas.edu/courses/old/310N/spring2008/ReactMoviesFI05%20SN2text.html>.