International Baccalaureate

Extended essay cover

Diploma Programme subject in which this extended essay is registered: __Chemistry__

(For an extended essay in the area of languages, state the language and whether it is group 1 or group 2.)

Title of the extended essay: _The Effects of Ultrasound on the Relative Yeild of Elimination and Substitution Mechanisms when Halogenoalkanes are Reacted with Sodium Hydroxide_

Candidate's declaration

If this declaration is not signed by the candidate the extended essay will not be assessed.

The extended essay I am submitting is my own work (apart from guidance allowed by the International Baccalaureate).

I have acknowledged each use of the words, graphics or ideas of another person, whether written, oral or visual.

I am aware that the word limit for all extended essays is 4000 words and that examiners are not required to read beyond this limit.

This is the final version of my extended essay.

Candidate's signature: _____ Date: 02/02/09

designed a unique and interesting research question which required the hire of ultrasound apparatus. The organization of which, required liaising with the school administration and the company. This delayed the start of collecting experimental data but he was still able to tackle the research question. This was based on good background knowledge of chemistry.

The research question was developed from work covered on the course on substitution and elimination reactions. It is suitable because it addresses how ultrasound could affect the relative yield of competing products and this is not considered on the course.

A problem was how to measure the relative yield given the limited equipment we have in school. choose to estimate this from mass changes caused by loss of the lower boiling point product by evaporation. Although this would not give very accurate results it showed real initiative from the student on using limited resources.

The report produced was not easy to follow. In places he uses non-scientific language and his description of making up a standard solution of sodium hydroxide confusing. The data tables appear overly complicated with no observations. Changes in the presentation could have improved the essay Although he shows some good basic chemistry theory in the early part of the essay, he does not relate this well to the results. Although aware of limitations his handling of error analysis is not appropriate. However, overall he has attempted some original work which I encouraged with some success.

Supervisor's report

The supervisor must complete the report below and then give the final version of the extended essay, with this cover attached, to the Diploma Programme coordinator. The supervisor must sign this report; otherwise the extended essay will not be assessed and may be returned to the school.

Name of supervisor (CAPITAL letters) _____

Comments

Please comment, as appropriate, on the candidate's performance, the context in which the candidate undertook the research for the extended essay, any difficulties encountered and how these were overcome (see page 13 of the extended essay guide). The concluding interview (viva voce) may provide useful information. These comments can help the examiner award a level for criterion K (holistic judgment). Do not comment on any adverse personal circumstances that may have affected the candidate. If the amount of time spent with the candidate was zero, you must explain this, in particular how it was then possible to authenticate the essay as the candidate's own work. You may attach an additional sheet if there is insufficient space here.

See attached sheet

I have read the final version of the extended essay that will be submitted to the examiner.

To the best of my knowledge, the extended essay is the authentic work of the candidate.

I spent ⎡ 4 ⎤ hours with the candidate discussing the progress of the extended essay.

Supervisor's signature: _____ Date: 30 / 01 / 2009

Extended Essay

-Chemistry-

The Effects of Ultrasound on the Relative Yield of Elimination and Substitution Mechanisms when Halogenoalkanes are Reacted with Sodium Hydroxide

Word Count: 3,751 ✓

December 2008

Contents

Abstract

This experiment investigated the research question: "How does the Utilization of Ultrasound Affect the Relative Yield of the Competing Elimination and Substitution Mechanisms in the Reaction of Bromobutane and Sodium Hydroxide to Form an Alcohol?"   ✓ RQ

Halogenoalkanes reacts with a salt containing a hydroxide ion to form an alcohol with the same structural descriptor (primary, secondary, or tertiary) as the original halogenoalkane. However, there are actually two competing reactions occurring: a substitution reaction forming the alcohol, and an elimination reaction forming an alkene. The relative yield is of interest because if ultrasound is used to catalyze competing reactions, it is desirable to know how the products are affected.

I chose to investigate the effects of ultrasound on this reaction because of ultrasound's ability to increase the rate and reactivity of reactions that are normally unfeasible at room temperature. Ultrasound's effect on the relative products from a halogenoalkane and sodium hydroxide reaction has little literature. This, as well as ultrasound's ability to thoroughly mix liquid reactants, lead me to investigate this research question.   Scope

In this experiment, ultrasonic radiation was employed for short intervals (about 0.5 sec every 4-5 sec.) during the reaction process. The mass lost by the evaporation of alkenes formed through elimination was measured. This loss in mass formed the basis of for the calculation of the relative yield of the two competing reactions. Using 10 separate trials for each of 3 different bromoalkane structures (1-bromobutane, 2-bromobutane, and 2-bromo-2-methyl propane), the average yield percentage for each was calculated. The yields of the primary, secondary, and tertiary bromoalkanes increased from 4% to 8%, 8% to 48%, and 76% to 89%, respectively, with the application of ultrasound to the reaction. It is   Concl. proposed that the heat equivalent of the ultrasound results in the increase in yield for the elimination reaction.

Word count: 298

Research Question

How does the Utilization of Ultrasound Affect the Relative Yield of the Competing Elimination and Substitution Mechanisms in the Reaction of Bromobutane and Sodium Hydroxide to Form an Alcohol or an Alkene?

Introduction

Halogenoalkanes exist in three main formations: primary, secondary, and tertiary forms. These forms can be reacted with sodium hydroxide creating primary, secondary, or tertiary alcohols, respectively, through a substitution reaction. This substitution reaction competes with an elimination reaction that produces an alkene. Specifically, the bromine becomes aqueous and a hydrogen is removed, which reacts with the hydroxide ion to form water.[1] Desiring to investigate an area of chemistry that was not widely reported and is more esoteric, I chose to investigate the effects of the addition of ultrasound on the yield of these competing reactions, This area is also new and unexplored as I could find no *Interesting* ✓ *Good initiative.* reference to ultrasound's effect on the relative yield of these reactions.

Because of ultrasound's catalytic nature, it was imperative that if it were to be used in an environment containing two competing reactions that it's effect on that competition be understood. In order to investigate this relationship, I chose a relatively complex reaction, but a relatively simple measurement protocol. When butene is formed by way of the elimination reaction, it vaporizes instantly because of its low boiling point, i.e., -6.3°C for but-1-ene, 3°C and 1.9°C for the cis and trans forms of but-2-ene, respectively, and -6.9°C for 2- ✓ methyl-propene.[2] Further, because all of the alcohols formed by the reaction have a boiling point greater than 80°C, there would be little anticipated loss of alcohol from boiling to create ✓ an error in the measurement. Thus, by measuring the mass lost when the reaction was complete, the theoretical yield of the alkene could be extrapolated. This loss of mass could be used as a basis for the calculation of the yield of the competing reactions. The basis of my discussion is, therefore, whether ultrasound has an effect, and if so, what is the degree of that effect on the reaction.

Succinct and to the point.

[1] - reference 1
[2] - reference 4

Background Information

Sonochemistry

Sonochemistry was discovered in the late 1800's, based upon observed erosion of propellers used on ships at that time. John I. Thornycroft and Sydney W. Barnaby were looking to explain and prevent this erosion, and observed the formation of large bubbles in the liquid around the propellers. It was these bubbles, these cavities, that formed the initial idea of Sonochemistry. As ships were improved and ship speeds increased, the deterioration caused by these cavities presented a threat to the British navy and their ships. Lord Rayleigh performed experiments to address this concern and conclusively investigate this phenomenon. He discovered that it was the collapse of the cavities that caused the destructive effects and that these cavities could be formed by high turbulence liquid motion as well as ultrasonic irradiation.[3]

The effects of this collapse are well tested and documented. The localized energy of these collapses is enormous, with a temperature equivalent of 5000°C and 1000 atmospheres of pressure.[4] This energy is the basis of ultrasound's unique effect on chemical reactions. Because of its high temperature equivalent, ultrasound is capable of catalyzing reactions. Furthermore, in solutions, the collapse of these cavities smash large numbers of molecules together, and according to collision theory, aid in the rate of reaction. In fact, for reactions where the mechanism is normally not feasible at room temperatures, the use of ultrasound can increase reactivity by over a million fold.[5]

Elimination vs. Substitution

During the formation of alcohols from halogenoalkanes and hydroxide ions, there are two competing reactions that occur. The first is a nucleophilic substitution reaction, which involves a relative positive region being attacked by a negative center; in this case hydroxide ions. The reaction follows one of two possible mechanisms.:

The first is S_N1, when the bromine breaks from its carbon, forming a carbo-cation with a positive center. This center is then attacked by the hydroxide ion, forming an alcohol by attaching to the now positive carbon.

The second mechanism is S_N2, involves the formation of an activated complex, which is an unstable transitory state, wherein both the bromine and hydroxide ions attached to the

[3] - reference 7
[4] - reference 8
[5] - reference 7

carbon. The bond with the bromine then breaks, releasing the bromine into the solution, with the final result again being an alcohol.[6]

The second and competing reaction in this case is an elimination reaction. As above, there are two possible mechanisms for this reaction: E1 and E2. Both mechanisms follow a mechanism similar to the substitution reaction with the same numerical coefficient.

The E2 reaction mechanism is characterized as an S_N2 mechanism where the negatively charged center does not attack the carbon at its positive center, but instead attacks one of the hydrogens. Because the electrons previously bonding the hydrogen and the carbon are now unbonded, the electrons form a double bond between that carbon and the carbon with the halogen attached to it, as that carbon has a greater positive charge due to the presence of a negative group attached to it. Due to these electrons forming this bond, the halogen is forced from its carbon.

The E1 mechanism, like the E2 mechanism, is a reflection of the opposing substitution mechanism. The halogen leaves in the rate determining step, followed by the negative ion attacking one of the hydrogens as above. And, also as above, the resulting unbounded electrons form a double bond between carbons.[7]

These two reactions work in terms of the structure of the organic molecule (primary, secondary, or tertiary) involved in the reaction. This can be explained by the fact that the mechanisms are determined by what positive center the nucleophile "attacks" during the reaction. For substitution reactions, the positive center that is attacked is a carbon atom, and for the elimination reaction the positive center attacked is a hydrogen atom[8]. The carbon is the positive center most common for primary halogenoalkanes, because the carbon that has bonded with the halogen is the most positive area, and is not tightly surrounded by other atoms, and is often attacked by the nucleophile. The tertiary halogenoalkane, on the other hand, is tightly surrounded by other atoms, meaning that often a hydrogen is attacked instead of a carbon, i.e., on the way to the positively charged carbon, a hydrogen is contacted and the collision triggers a reaction.

Different conditions needed. Ethanol for elimination, H_2O for Substitution. OH acting as a base? Also heat needed. The discussion is incomplete without this.

[6] - reference 1
[7] - reference 2
[8] - references 1 & 2

Chart 1: SN1 Mechanism Example

Reactants   Intermediate carbocation   Products

Rate limiting step involves just one molecule

Extremely rapid

$$R = k[(CH_3)_3CBr]$$
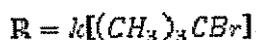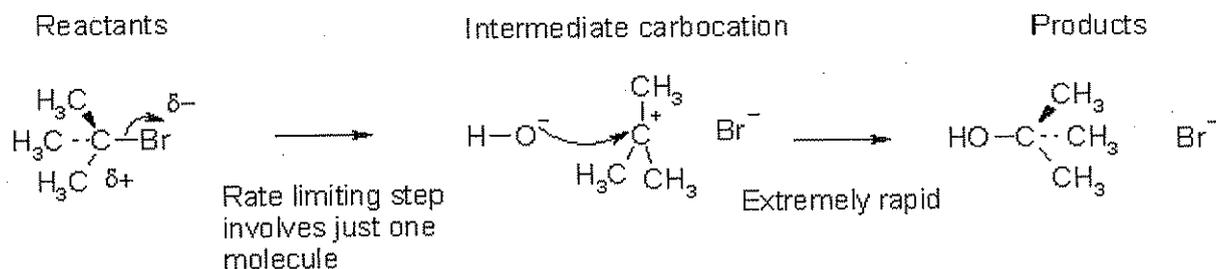
Chart 2:SN2 Mechanism Example

Reactants   Intermediate carboanion   Products

Rate limiting step involves two molecules

Extremely rapid

$$R = k[CH_3Br][OH^-]$$
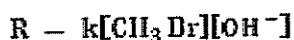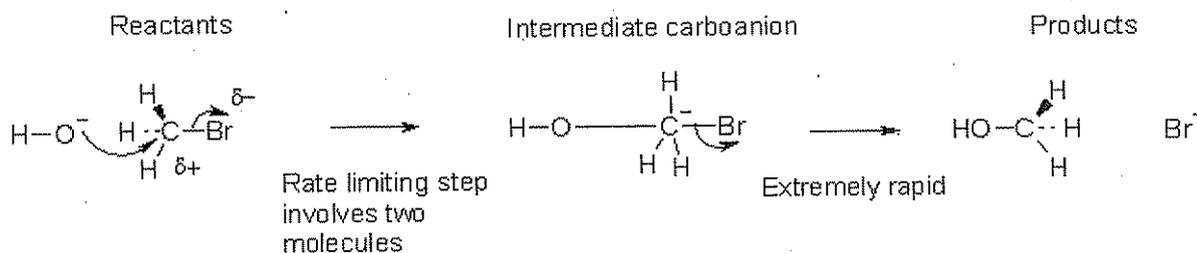
Chart 3: E1 Mechanism Example

Reactant   Intermediate Carbocation   Products

Rate determining step Involves one molecule

Extremely rapid

$$R = k[CH_3CH_2CCH_3BrCH_3]$$

Chart 4: E2 Mechanism Example

Reactants   Products

Rate determining step
Involves two molecules

$$R = k[CH_3CH_2CCH_3BrCH_3][OH^-]$$

First two pictures: www.steve.gb.com

Second two pictures: www.chemhelper.com

Procedural Write-Up

1. Fill two 100 cm³ volumetric flasks with distilled water. To these flasks, add 0.399 grams of NaOH and 1.699 grams of silver nitrate in order to form 1 molar solutions of both the NaOH and the silver nitrate

2. Prepare four test tubes at a time, using a pipette to add 2 cm³ of the bromoalkane. Record the mass of the test tube and the organic added.

3. Add, using a pipette, 3 cm³ of ethanol to the solution. Shake thoroughly, as the ethanol will act as the solvent that brings all the reactants in contact with one another. Again, record the mass of the test tube.

4. Mass a test tube, and add 2 cm³ of silver nitrate to that test tube. Take the new mass with the silver nitrate and subtract in order to measure the mass of the silver nitrate. Add the 2 cm³ of the silver nitrate to the test tube in which the reaction is to take place.

5. Measure the mass of a separate test tube, add 2.5 cm³ of NaOH to that test tube. Record the mass of the NaOH solution by massing that same test tube with the NaOH inside it and taking the difference.

6. Now add the 2.5 cm^3 of the NaOH solution to begin the reaction. Record a value in your data table equal to the mass of the test tube with the ethanol and the bromoalkane plus the mass of the silver nitrate plus the mass of the sodium hydroxide.

7. Using the formation of silver bromide (a yellow solid) as a measure for completion, wait until the reaction is complete.

8. Once the reaction is complete, take the mass of the test tube. The difference of the masses recorded before the reaction took place and the mass of the final solution after the reaction has taken place will be equal to the alkene produced.

9. Repeat 9 times more

10. Repeat steps 1-9 ten additional times, with one adjustment. Between steps 7 and 8, apply ultrasound using a setup as seen in the appendix. Apply 9-10 times for about 0.5 seconds each time, spaced out over about 15 to 20 seconds, to prevent sonotrode from heating and boiling off reactants or products other than the alkene.

Procedure as it was Carried out

Both the primary and tertiary organic reactions were carried out according to this method; however the secondary organic reaction was done slightly differently as it was the first reaction carried out. Because it was first, the method had not been perfected, and therefore there was significant time loss in performing these reactions. Nonetheless these results are not to be disregarded.

For the secondary reaction, silver nitrate was used in solution but the sodium hydroxide remained solid, in powdered form, during the reaction. Also, the only solvent used was water, thus creating a barrier between the organic and the slowly dissolving sodium hydroxide, as the organic was insoluble in water. Therefore the reactants did not mix fully. Ultimately the reaction time lasting longer than 20 minutes for each of the non-ultrasound catalyzed reactions. It should be noted that all catalyzed reactions were fully reacted after

approximately 10-15 seconds of ultrasonic radiation exposure, supporting the conclusion that ultrasound will serve to mix liquid reactants fully.

Investigation of the Primary Organic

Hypothesis formed

According to literature regarding the reaction mechanisms of elimination and substitution reactions one would expect that the addition of ultrasound will result in a higher yield for the elimination reaction. This hypothesis was formed because it is noted in the literature that elimination reactions have a greater yield when heat was add, and heat is the primary effect of the addition of ultrasound found in the research above.[9]

√ yes.

$$CH_2BrCH_2CH_2CH_3 + NaOH_{(aq)} \rightarrow CH_2OHCH_2CH_2CH_3 + Na^+_{(aq)} + Br^-_{(aq)}$$
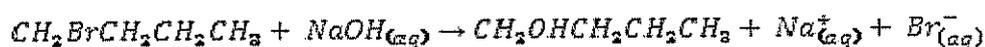
Equation 1: Substitution reaction to form a primary alcohol

$$CH_2BrCH_2CH_2CH_3 + NaOH_{(aq)} \rightarrow CH_2CHCH_2CH_3 + H_2O + Na^+_{(aq)} + Br^-_{(aq)}$$
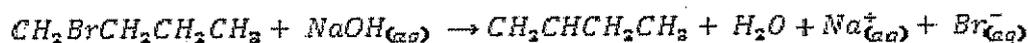
Equation 2: Elimination reaction to form an alkene

1-bromobutane was reacted with powdered sodium hydroxide as the hydroxide ion is a strong nucleophile, which is necessary for either of the reactions shown above. In order to determine when the reaction was complete, silver nitrate was added, as silver bromide will form, signaling that the reaction is still in progress. Upon completion, no new silver bromide will form, a noticeable change as silver bromide forms quite visibly, with a fizzing reminiscent of soda water. Further, the solution of 2-bromobutane and silver nitrate is a yellow color, while silver bromide is a brown color, and quite dark. Ten trials with ultrasound and ten trials without ultrasound were preformed, with the data recorded in the following chart:

?

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[9] - Reference 7

Table 1: experimental data of primary halogenoalkane

Trial	gramsNaOH± 0.0100	grams AgNO$_3$± 0.005	Grams C$_4$H$_9$Br ± 0.005	MolsNaOH± 0.000141	Mols AgNO$_3$± 0.0000155	Mols C$_4$H$_9$Br ± 0.0000188	Initial Grams of everything ± 0.0200	Final Grams of everything ± 0.005	Grams lost ± 0.0250	Mols C$_4$H$_8$± 0.000838
1	1.00	0.810	2.35	0.0251	0.00480	0.0141	8.65	8.63	0.0200	0.000356
2	1.00	0.890	2.54	0.0251	0.00527	0.0152	8.92	8.90	0.0200	0.000356
3	1.00	0.880	3.42	0.0251	0.00521	0.0205	9.79	9.78	0.0100	0.000178
4	1.00	0.820	3.87	0.0251	0.00486	0.0232	10.2	10.1	0.0800	0.00143
5	1.00	0.830	4.12	0.0251	0.00491	0.0248	10.4	10.4	0.0500	0.000891
6	.00	0.900	4.45	0.0251	0.00538	0.0266	10.8	10.8	0.0900	0.00160
	1.00	0.790	5.3	0.0251	0.00468	0.0317	11.6	11.5	0.0800	0.00143
8	1.00	0.840	5.71	0.0251	0.00497	0.0342	12.0	11.9	0.160	0.00285
9	1.00	0.860	6.01	0.0251	0.00509	0.0360	12.4	12.3	0.110	0.00196
10	1.00	0.840	6.34	0.0251	0.00497	0.0380	12.7	12.6	0.070	0.00125
1 US	1.00	0.910	2.44	0.0251	0.00539	0.0146	8.8	8.8	0.000	0.000
2 US	1.00	0.840	2.65	0.0251	0.00497	0.0159	9.0	8.9	0.0800	0.00143
3 US	1.00	0.880	3.15	0.0251	0.00521	0.0189	9.5	9.4	0.120	0.00214
4 US	1.00	0.770	3.65	0.0251	0.00456	0.0219	9.9	9.8	0.100	0.00178
5 US	1.00	0.790	3.92	0.0251	0.00468	0.0235	10.2	10.0	0.170	0.00303
6 US	1.00	0.850	4.23	0.0251	0.00503	0.0253	10.6	10.4	0.200	0.00356
7 US	1.00	0.810	4.66	0.0251	0.00480	0.0279	11.0	10.8	0.130	0.00232
8 US	1.00	0.890	5.08	0.0251	0.00527	0.0304	11.5	11.3	0.140	0.00250
9 US	1.00	0.910	5.98	0.0251	0.00539	0.0358	12.4	12.3	0.110	0.00196
) US	1.00	0.900	6.23	0.0251	0.00533	0.0373	12.6	12.4	0.210	0.00374

As can be seen from the data in Table 1, it appears that the hypothesis formed is supported by the experimental evidence. This can be seen in the fact that the amounts of alkene formed during the reaction catalyzed by the ultrasound were consistently higher than the amounts formed during the reaction without ultrasound. Since the observed results without ultrasound are consistent with the literature, the observations with ultrasound are considered to be compelling. For example, according to experimental data, primary halogenoalkanes undergo primarily substitution based reactions to form alcohols much more readily than they undergo elimination reactions. This observation matches the literature. In this case there was an average of a 4% ± 0.00727% yield to butene when there was no

ultrasound used, based on a mol to mol ratio in the reaction equation. A 4% yield is sufficiently small to support the fact that the reaction is mainly a substitution reaction.

If the hypothesis is true, the percentage yield to the elimination reaction should increase significantly (for example, a doubling of the yield from 4 to 8 % would be a significant increase in yield), in order to confirm that any increase in the yield is unlikely to have been caused by anything other than the addition of ultrasound. The final average yield of the ultrasound catalyzed reaction was 9% $\pm$ 0.0134%, which is more than a 5% increase and thus, a statistically significant increase, supporting the hypothesis that an ultrasound catalyzed reaction increases yield of the elimination reaction.

Investigation of the Secondary Organic

It is within the investigation of secondary organics that the largest difference between the yield of the elimination reaction, with and without the ultrasound, was expected. This expectation is based upon the fact that secondary compounds, according to literature, are the most likely to be a combination of both elimination reactions and substitution reactions and also the easiest in which to cause a shift in the reaction mechanism.[10]

$$CH_3CHBrCH_2CH_3 + NaOH \rightarrow CH_3CHOHCH_2CH_3 + Na^+ + Br^-$$
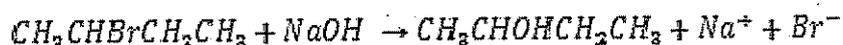
Equation 3: Substitution Reaction to form a secondary Alcohol

$$CH_3CHBrCH_2CH_3 + NaOH \rightarrow CH_2CHCH_2CH_3 + H_2O + Na^+ + Br^-$$
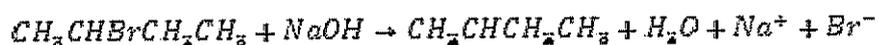
subscripts not very clear

Equation 4: Elimination Reaction to form an alkene

In this reaction, 2-bromobutane was reacted with powdered sodium hydroxide and a silver nitrate solution. There was no ethanol solvent in this reaction, and therefore the reaction time was enormous, even when subjected to consistent shaking. This reaction took on average 20 to 25 minutes to complete, and may not have fully reacted. This as well as the fact that the sodium hydroxide needed time to dissolve in the water, because it began in powdered form, could cause some subtle differences between the results seen here and those seen for the primary and the tertiary organic compounds. As with the primary organic compound, there were ten trials with ultrasound and ten trials without. The data can be seen in the chart below:

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[10] – Reference 3

Table 2: Data collected involving the Secondary Organic Compound

Trial	gramsNaOH± 0.0100	grams AgNO$_3$± 0.005	Grams C$_4$H$_9$Br ± 0.005	MolsNaOH± 0.000141	Mols AgNO$_3$± 0.0000150	Mols C$_4$H$_9$Br ± 0.0000189	Initial Grams of everything ± 0.0200	Final Grams of everything ± 0.005	Grams lost ± 0.0250	Mols C$_4$H$_8$± 0.000226
1	1.00	0.240	2.56	0.0251	0.00142	0.0153	3.80	3.77	0.030	0.000535
2	1.00	0.270	3.44	0.0251	0.00160	0.0205	4.71	4.66	0.050	0.000891
3	1.00	0.240	3.78	0.0251	0.00142	0.0226	5.02	4.98	0.040	0.000713
4	1.00	0.250	3.93	0.0251	0.00148	0.0235	5.18	5.12	0.060	0.00107
5	1.00	0.240	4.17	0.0251	0.00142	0.0250	5.41	5.36	0.050	0.000891
6	1.00	0.250	4.55	0.0251	0.00148	0.0272	5.80	5.73	0.070	0.00125
7	1.00	0.250	4.66	0.0251	0.00148	0.0279	5.91	5.87	0.040	0.000713
8	1.00	0.260	4.96	0.0251	0.00154	0.0297	6.22	6.13	0.090	0.00160
9	1.00	0.250	5.45	0.0251	0.00148	0.0326	6.70	6.60	0.100	0.00178
10	1.00	0.260	6.34	0.0251	0.00154	0.0380	7.60	7.49	0.110	0.00196
1 US	1.00	0.250	2.54	0.0251	0.00148	0.0152	3.79	3.19	0.600	0.0107
2 US	1.00	0.250	2.98	0.0251	0.00148	0.0178	4.23	3.60	0.630	0.0112
3 US	1.00	0.270	3.51	0.0251	0.00160	0.0210	4.78	4.21	0.570	0.0102
4 US	1.00	0.240	3.77	0.0251	0.00142	0.0226	5.01	4.26	0.750	0.0134
5 US	1.00	0.270	3.99	0.0251	0.00160	0.0239	5.26	4.62	0.640	0.0114
6 US	1.00	0.250	4.31	0.0251	0.00148	0.0258	5.56	4.89	0.670	0.0119
7 US	1.00	0.240	4.88	0.0251	0.00142	0.0292	6.12	5.43	0.690	0.0123
8 US	1.00	0.240	5.01	0.0251	0.00142	0.0300	6.25	5.54	0.710	0.0127
9 US	1.00	0.260	5.63	0.0251	0.00154	0.0337	6.89	6.01	0.880	0.0157
0 US	1.00	0.250	6.32	0.0251	0.00148	0.0378	7.57	6.72	0.850	0.0151

As seen from the data in Table 2 derived from the investigation of the secondary organic compound, it is fairly clear that the addition of ultrasound to the reaction of a halogenoalkane and sodium hydroxide results in an increase in the yield of the elimination reaction. In this case, as in the case in Table 1 above, there was a clear and consistent increase in the mols of alkene produced with the application of ultrasonic radiation versus the mol of alkene produced without such a catalyst. In this case, the percentage yield in the elimination reaction without the ultrasound was found to be 8% ± 0.0132%. As previously discussed above, there needs to be a significant increase in the percentage yield in the elimination reaction in order for the results of the lab to be deemed significant results. In this case the increase of the reaction is to 48% ± 0.757%..

As predicted, there was a very significant increase in the percentage yield of the elimination reaction. This is in part, due to how easily the reaction that occurs in secondary halogenoalkanes can be shifted between elimination and substitution reactions. Because the secondary halogenoalkanes have a structure that allows negative centers an equal opportunity to attack hydrogens as to attack the halogeno-functional group, both reactions occur simultaneously, normally to the same degree. However in this case, there was only an 8% yield for the elimination when the ultrasound was not present. The reason for this lower yield and the inequality between the two reactions is because the presence of water as a solvent deters the elimination reaction and aids the substitution reaction. This was corrected in the primary and tertiary reactions by adding a small amount of an organic solvent, ethanol, which promotes the elimination reaction and opposes the substitution reaction. Together, the use of both these solvents results in a relative net gain while not affecting the reaction yield to any great degree. But in this case, water was the only solvent present, and affected the reaction accordingly.

The Effects of Ultrasound on the Relative Yield of Elimination and Substitution Mechanisms when Halogenoalkanes are Reacted with Sodium Hydroxide

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Investigation of the Tertiary Organic Compound

In the investigation of the tertiary organic, the literature states that there should be the largest yield in the elimination reaction of all three types of halogenoalkanes. It should be mentioned that while the compounds used in the past reactions were both forms of butane, the compound that was reacted in this case was a form of propane, specifically 2-bromo-2-methyl propane.

irrelevant only because of IUPAC naming they are all isomers of C_4H_9Br

$$CH_3CBrCH_3CH_3 + NaOH \rightarrow CH_3COHCH_3CH_3 + Na^+ + Br$$
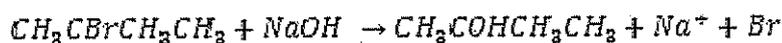
Equation 5: Substitution reaction to form a methyl-alcohol

$$CH_3CBrCH_3CH_3 + NaOH \rightarrow CH_2(C)CH_3CH_3 + Na^+ + Br^- + H_2O$$
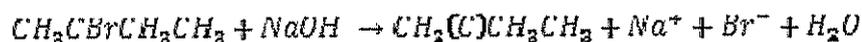
Equation 6: Elimination reaction to form a methyl-alkene

In selecting a tertiary compound, I was faced with two choices, either use a methyl butane to keep a butane chain involved in the reaction, or use methyl propane, and keep the same number of total carbon atoms involved. It was decided that keeping the same number of carbons involved in the reaction was more important that keeping the same chain length in the reaction. But as such, there was a different alkene formed in the final reaction, specifically a methyl propene. This change had no net effect on the experiment, as the boiling point of methyl propene, the characteristic necessary to measure weight change, is actually 9°C lower than that of butane, and thus did not affect the measurement of the yield in the elimination reaction. It boiled away as the alkenes did in the previous experiments.

an isomer of butene!

As with the prior reactions, there were ten trials without ultrasonics, and ten that included ultrasonics. The recorded data appears below:

Table 3: experimental data of the tertiary halogenoalkane

Trial	gramsNaOH± 0.0100	grams AgNO$_3$± 0.005	Grams C$_4$H$_9$Br ± 0.005	MolsNaOH± 0.000141	Mols AgNO$_3$± 0.0000155	Mols C$_4$H$_9$Br ± 0.0000189	Initial Grams of everything ± 0.0200	Final Grams of everything ± 0.005	Grams lost ± 0.0250	Mols C$_4$H$_8$± 0.000232
1	1.00	0.840	2.28	0.0251	0.00497	0.0137	8.61	8.03	0.58	0.0103
2	1.00	0.880	2.79	0.0251	0.00521	0.0167	9.16	8.34	0.82	0.0146
3	1.00	0.900	3.25	0.0251	0.00533	0.0195	9.64	8.78	0.86	0.0153
4	1.00	0.910	3.77	0.0251	0.00539	0.0226	10.2	9.29	0.88	0.0157
5	1.00	0.810	4.01	0.0251	0.00480	0.0240	10.3	9.31	1.00	0.0178
6	1.00	0.920	4.33	0.0251	0.00545	0.0259	10.7	9.52	1.22	0.0217
7	1.00	0.790	4.79	0.0251	0.00468	0.0287	11.1	10.0	1.07	0.0191
8	1.00	0.870	5.37	0.0251	0.00515	0.0322	11.7	10.4	1.34	0.0239
9	1.00	0.930	5.73	0.0251	0.00551	0.0343	12.2	10.6	1.60	0.0285
10	1.00	0.830	6.22	0.0251	0.00491	0.0372	12.5	11.1	1.44	0.0257
1 US	1.00	0.880	2.22	0.0251	0.00521	0.0133	8.59	7.93	0.66	0.0118
2 US	1.00	0.800	2.43	0.0251	0.00474	0.0146	8.72	7.94	0.78	0.0139
3 US	1.00	0.870	3.10	0.0251	0.00515	0.0186	9.46	8.54	0.92	0.0164
4 US	1.00	0.750	3.97	0.0251	0.00444	0.0238	10.2	9.12	1.09	0.0194
5 US	1.00	0.790	4.15	0.0251	0.00468	0.0249	10.4	9.23	1.20	0.0214
6 US	1.00	0.830	4.85	0.0251	0.00491	0.0290	11.2	9.79	1.38	0.0246
7 US	1.00	0.850	5.23	0.0251	0.00503	0.0313	11.6	9.93	1.64	0.0292
8 US	1.00	0.770	5.79	0.0251	0.00456	0.0347	12.0	10.4	1.64	0.0292
9 US	1.00	0.830	6.04	0.0251	0.00491	0.0362	12.4	10.6	1.72	0.0307
US	1.00	0.880	6.35	0.0251	0.00521	0.0380	12.7	10.6	2.10	0.0374

During the trials for the tertiary compounds, detection of a change in the number of grams lost between the trials that used no ultrasound and the trials that used ultrasound was called into question. Specifically, the great loss of mass during the trials that did not use the ultrasound raised a concern that there would not be enough of a detectable change between the two to yield a significant result. The yield of the elimination reaction where no ultrasound was applied was 76% ± 0.930%. This yield increased in its average despite fears that it might be immeasurable. With the application of ultrasound, the percentage yield increased to 89% ± 0.766%. This change was considered significant because the percentage yield increased by a greater degree in this experiment than in the previously discussed investigation of the primary halogenoalkanes (5% to 13%).

Conclusion

Based upon the data, that the addition of ultrasonic radiation to a reaction between any of a primary, secondary or tertiary halogenoalkane and a nucleophile will result in an increased yield in the elimination reaction and a decreased yield in the substitution reaction. This result is especially true for a secondary halogenoalkane, and thus, if the desire is to increase the yield of the alkene being produced without producing a methyl-alkene, a secondary halogenoalkane with an ethanol solvent should be reacted with a nucleophile under the addition of ultrasound.

Evaluation

Random Error: Error in all mass measurements was $\pm$ 0.005g; the errors in the sum of the mass of each of the reactants was $\pm$ 0.015g; the error on the mass lost was 0.02g; and the error on the molar quantities of both the alkene/methyl-alkene formed and the reactants were variable dependant on the masses involved, but ranged from $\pm$ 0.000831 to $\pm$ 0.00268. The values provided in the tables above are the average error of the data.

Systematic Error: It was often difficult to determine exactly when the reaction had reached completion, due primarily to the observed varied characteristics of the end-detection method used, silver nitrate. Hence it was felt that if the reaction had been left longer, it might have reacted further resulting in additional loss of mass due to the evaporation of additional alkene. This is an error that, while meriting mention, does not affect the conclusions of this investigation. This investigation seeks to determine what effect there is on the competing reactions, elimination and substitution, with the addition of ultrasound, and the relative yields of each. Since the numeric results indicate that ultrasound moves the competing reactions toward elimination, and further since the relative yields are all statistically significant, the impact of ending any reaction early would merely be on the relative yield of the elimination product for that trial. Thus, the conclusion that ultrasound moves all of primary, secondary, and tertiary halogenoalkanes toward elimination is not undermined by this error.

It is also important to note that sonotrodes are notoriously difficult to clean. This is because a sonotrode is not allowed to be cleaned with anything corrosive or bleach based, as this might contaminate the future reactions to catalyzed by this sonotrode. Thus, the only option available in the school lab was distilled water, which is not an ideal cleaning agent. Despite thorough cleaning, there was evidence of contaminated reactions, such as odd colors present in the reaction, or a separate layer of material that did not mix with the other

materials. Contamination caused me to question the validity of certain trials. Therefore, 10 trials were preformed as opposed to the originally anticipated 4 trials. It was decided that doubling the number of trials, in addition to cleaning the sonotrodes as thoroughly as was possible, would render the flaw to the results negligible.

The final error, probably the most important, is that the sonotrode heats up during the addition of ultrasound to the reaction. According to it's instruction manual, the sonotrode can increase to a maximum of 500°C after about one minute of constant ultrasound application. This temperature would be able to boil the water/ethanol solvents, as well as the alcohol formed through these reactions, which would render the results worthless. So in order to avoid this result, the sonotrode was applied in short bursts, usually for about half a second every four or five seconds. This inconsistent use should have negated the temperature increase almost entirely. According to a thermometer check immediately after such a use, the temperature was quickly falling from about 45°C when the reading was taken, approximately 1 second after the sonotrode was deactivated. This seems rather high, as the sonotrode began at room temperature, and thus it is possible that a small amount of the other reactants or products were boiled away as well.

Literature Errors: It was decided that Internet sources were the most pertinent to this investigation due to the general difficulty in finding written literature that was relevant. Particularly it was difficult to find any articles describing specific, rather than general, uses of sonochemistry for chemical catalysis. There are not many studies on this topic, including few references in our school library. On the other hand, due to the internet's nature as a free source, much of the data must be verified. Thus, for all internet sites, no information was quoted or used in the investigation unless taught by a chemistry teacher, written in a text book in support, or verified on at least two, preferably three, different internet sources.

An original topic and a very interesting EE to read. Shows much initiative and the use of measuring loss in mass due to evolution of alkene is simple, but elegant and effective in this context. A more thorough understanding of the elimination reaction, different conditions etc would have helped the discussion.

Sample Calculations

Molar calculations :
$$\frac{grams}{\frac{grams}{mol}} = mols, ex \quad \frac{0.02\ g}{56.11\ gmol^{-1}} = 0.000356\ mol$$

Addition Error Calculations: $error\ 1 + error\ 2 = error\ 3, ex.\ 0.005 + 0.005 = 0.010$

Error Calculations for Mols of Alkene:

$$\frac{mass\ lost}{error_{(mass\ lost)}}\ x\ (mols\ alkene) = Error\ on\ Mols\ of\ alkene$$

$$ex.\frac{0.02}{0.03}\ x\ 0.000535 = 0.000356, \quad thus\ mols\ of\ alkene = 0.000535 \pm 0.000356$$

Error Calculations for percent yield:

$$\left(\frac{error_{(mols\ alkene)}}{mols\ alkene} * \frac{Mols\ of\ alkene}{Mols\ of\ bromoalkane}\right) * 100 = Percent\ error$$

$$ex.\frac{0.000356}{0.000535} * \frac{0.000535}{0.015329} = 0.023252 * 100 = 2.3252\%\ error$$

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Appendix

Apparatus List

- 100 cm³Volumetric Flask (x1)
- 200 cm³ Beaker (x2)
- Test tube (x7)
- Test tube stopper (x7)
- Pipette (x1)
- Ultrasound Generator (x1)
- Sonotrode (x1)
- Metal Spatula (x1)
- Clamp Stand (x2)
- Clamps (x2)
- Digital Mass Measure (x1)
- 100°C Thermometer (x1)
- Watch Glass (x1)
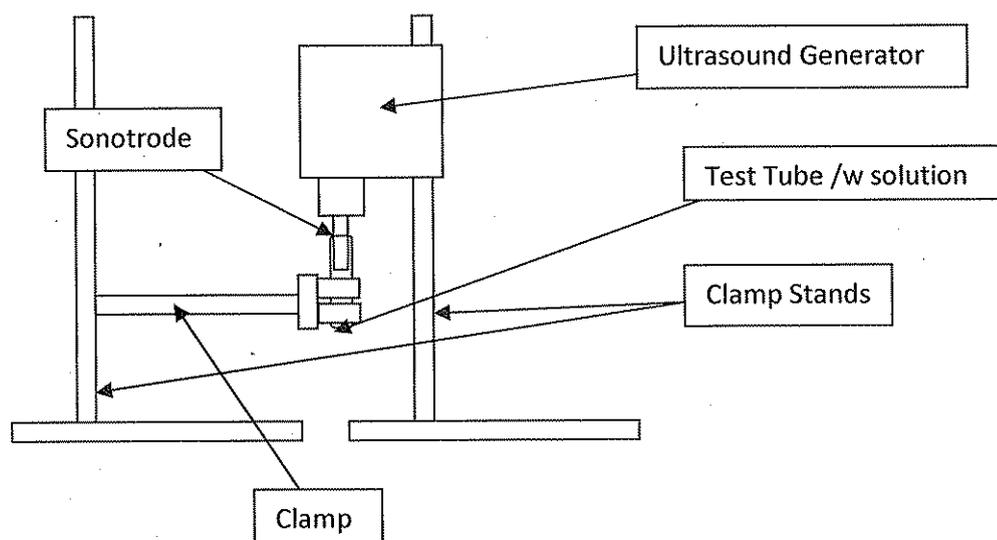
Chart 5: Ultrasound Apparatus Set-up

Reactants and Product Compound's Relevant Information

Silver Nitrate
Reacts with the bromide ion to form silver bromide, a visible yellow solid used to measure reaction completion.
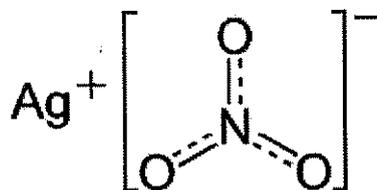
1-Bromobutane
Primary Halogenoalkane
Boiling Point = 101.4°C

2-Bromobutane
Secondary Halogenoalkane
Boiling Point = 91°C
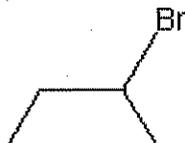
### 2-Bromo-2-methyl Propane
Tertiary Halogenoalkane
Boiling Point = 73°C
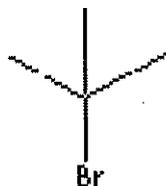

Butan-1-ol
Primary Alcohol
Boiling Point = 117.73°C

But-1-ene
Boiling Point = -6.3°C

Butan-2-ol
Secondary Alcohol
Boiling Point = 94°C
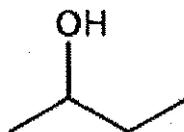

But-2-ene
Boiling Point = 1°C
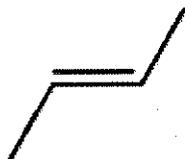
2-methylpropan-2-ol
Tertiary Alcohol
Boiling Point = 82.4°C
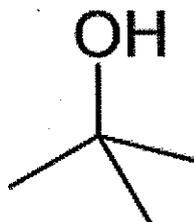
2-methylpropene
Boiling Point = -6.9°C
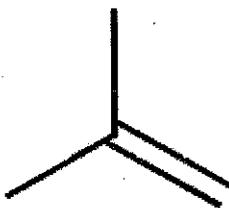
Sodium Hydroxide
Reacts with the organic,
providing the neucleophile (OH⁻ ion)
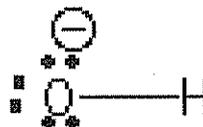
Assessment form (for examiner use only)

Candidate session number	

Achievement level

Assessment criteria

		First examiner	maximum	Second examiner
A	research question	2	2	
B	introduction	2	2	
C	investigation	4	4	
D	knowledge and understanding	3	4	
E	reasoned argument	3	4	
F	analysis and evaluation	4	4	
G	use of subject language	3	4	
H	conclusion	2	2	
I	formal presentation	4	4	
J	abstract	2	2	
K	holistic judgment	4	4	

Total out of 36   33

ame of first examiner: _____   Examiner number: _____
CAPITAL letters)

ame of second examiner: _____   Examiner number: _____
CAPITAL letters)