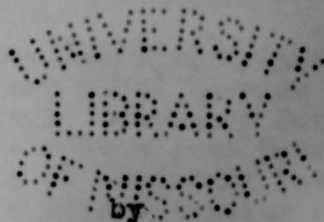


THE REACTION OF METALLIC HYDROXIDES
ON SECONDARY BUTYL BROMIDE



Walter William Johler, B. S.

SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS

in the

GRADUATE SCHOOL

of the

UNIVERSITY OF MISSOURI

1933

*Approved.
H. P. Smith*

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	4
III. EXPERIMENTAL	10
A. Preparation and Purification of Secondary Butyl Bromide	10
B. Hydrolysis of Secondary Butyl Bromide with Silver Hydroxide	12
C. Hydrolysis of Secondary Butyl Bromide with Potassium Hydroxide	12
D. Hydrolysis of Secondary Butyl Bro- mide with Sodium Hydroxide	14
E. Hydrolysis of Secondary Butyl Bro- mide with Calcium Hydroxide	14
F. Hydrolysis of Secondary Butyl Bro- mide with Barium Hydroxide	15
IV. SUMMARY	22
V. BIBLIOGRAPHY	23
VI. ACKNOWLEDGEMENT	24

INTRODUCTION

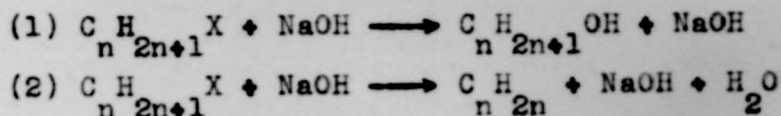
The alkyl halides are among the most important of the synthetic reagents of organic chemistry, due to the ease with which they enter into chemical reaction with many other substances. The chemical properties of this group of compounds have therefore been extensively studied. Most of this work has been qualitative in nature, though in recent years considerable attention has been given to quantitative measurements of their reactivity. Conant, Kirner, and Hussey¹ studied a variety of halogen compounds, measuring the rates of replacement of certain halogens by iodine, using potassium iodide or sodium iodide in acetone solution. Toward this reagent, the primary halide proved to be the most reactive, and the tertiary the least reactive. This particular reaction was selected because it gave the same type of product with a large variety of halogen compounds and was relatively free from side reactions. Slator² measured the rate of reaction between organic halides and sodium thiosulphate in water and in mixtures of alcohol and

1. J. Amer. Chem. Soc., 47, p. 488 (1925).

2. J. Chem. Soc., 103, p. 1689 (1913).

water, and obtained results which compared favorably with those of Conant. Nicolet and Stevens³ carried out the hydrolysis of various alkyl halides in neutral alcohol solution and found that secondary halides showed a more rapid reaction than the corresponding primary halides. Noller and Dinsmore⁴ studied the reactions of alkyl bromides with pyridine and reported that the removal of hydrogen bromide and quaternary salt formation were two simultaneous independent reactions.

This study is part of a comprehensive investigation of the hydrolysis of various types of alkyl halogen compounds. The action of the hydrolytic agents on alkyl halides generally results in the simultaneous formation of two different types of products, alcohols and olefine hydrocarbons. The alcohols are formed by hydrolysis and are usually the chief products, while the olefines are obtained through the elimination of halogen acid and generally represent side reactions. The equations representing these reactions are as follows:



3. J. Amer. Chem. Soc., 50, p. 135 (1928).

4. Ibid., 54, p. 1025 (1932).

The purpose of this investigation was to find the relative amounts of alcohol and olefine hydrocarbon produced on the hydrolysis of secondary butyl bromide using different hydrolytic agents under varying conditions of temperature and of concentration of the hydrolytic agents.

DISCUSSION

The hydrolytic reagents used in this work were the hydroxides of silver, potassium, sodium, calcium, and barium. Aqueous suspensions of silver, calcium, and barium hydroxides were used, so that the solutions were saturated at all times with the reagents. In most of the reactions 500 cc. of aqueous solution or suspension were used with about 12 grams of the secondary butyl bromide. With 25% potassium hydroxide only 200 cc. of the solution were used. In all reactions the hydroxide was used in excess.

The reactions were carried out in a liter pyrex round bottom flask provided with a tight rubber stopper fitted with a reflux condenser, a mercury seal motor stirrer, and a short piece of glass tubing closed at the outer end by means of a short rubber tube and a screw clamp. The butyl bromide was introduced into the reaction flask through this tube. The condenser served to condense the secondary butyl bromide which may have volatilized during the reaction, and return it to the reaction flask. The end of the condenser was provided with a trap, and a delivery tube which led to a three liter flask where the gaseous olefine hydrocarbons were

collected by the displacement of water. The reaction flask was heated to the desired temperature and then immersed in a large water bath which was maintained at the same temperature. The secondary butyl bromide was then pipetted into the reaction flask through the glass tube mentioned above. At the end of the reaction the residue of olefine was forced into the receiver by filling the reaction flask with water through the trap at the top of the condenser. The olefine remaining in the condenser and in the delivery tube was then swept out by passing air into the flask through the same tube by which the secondary butyl bromide was introduced.

The approximate time of the reaction was estimated by the period through which the olefine hydrocarbon was produced. This time does not have any great significance because the force of agitation, which could neither be measured nor kept constant, was one of the factors which affected the speed of the reaction, as well as did the reagent and the temperature. In all cases the heating and stirring were continued for an hour or more after the formation of the olefine hydrocarbon had ceased. Continuing the hydrolysis for a period of ten to fifteen times that of the period of olefine formation did not bring the reaction to completion.

In no case did the reaction go to completion, although careful precautions were taken to insure thorough mixing of the reacting substances. In one reaction with silver hydroxide at 60° the bromide was introduced directly into the flask so as to eliminate the possibility of any of it remaining in the short glass tube through which it had previously been introduced into the reaction mixture. About every thirty minutes throughout the reaction, 20-25 cc. of water heated to 60° were introduced through the trap in the top of the condenser into the reaction mixture. This was done to remove any bromide which may have condensed and carry it back into the reaction mixture. At the end of fourteen hours the reaction flask was full, so that there was no need of adding any more water through the condenser in order to force out the remaining olefine. The entire contents of the flask then had been in contact with the silver hydroxide and there was no way for any of the butyl bromide to be present except in contact with the silver hydroxide solution. The reaction was run for a total of fifteen hours, while the time of olefine formation was only three-fourths hours.

The reaction temperatures with silver hydroxide were 30°, 50°, and 60°. The temperatures used with

potassium hydroxide were 50° and 60° , and with sodium, calcium, and barium hydroxides the temperature was 60° . At any lower temperatures these last three reagents reacted so slowly as to be unsatisfactory.

The alcohol was recovered by the distillation of the reaction mixtures after they had been made neutral to phenolphthalein using nitric acid. A graph had been made previously in which concentrations of aqueous solutions of secondary butyl alcohol were plotted against refractive index. These aqueous solutions of the secondary butyl alcohol were made up by weighing alcohol and then water into a tared flask. The refractive index was determined by means of an Abbe refractometer that read accurately to the fourth decimal place. The results are given in Table I. This graph was to be used in determining the weights of the recovered alcohol from the various reactions. In no case, however, did complete reaction occur, so that the alcohol was always contaminated with small amounts of the secondary butyl bromide which made it impossible to use this method of analysis. The general plan followed was to determine the amount of olefine and the total weight of metal bromide. The metallic bromide equivalent to the olefine, when subtracted from the total amount of bromide formed, gave the weight

of bromide equivalent to the alcohol, from which the actual weight of alcohol could be calculated.

The olefine was measured by passing the mixture of air and olefine through fuming sulphuric acid, the loss representing the volume of olefine. For this analysis an Orsat gas analysis apparatus was used.

The analysis for the metallic bromides (except in the cases in which silver hydroxide was used) were carried out by diluting the reaction mixtures to a known volume and titrating aliquot portions with standard silver nitrate solution. The silver bromide was determined by dissolving the excess silver oxide in boiling nitric acid and weighing the washed silver bromide in a Gooch crucible.

The time of the reactions varied from three-fourths hours with silver hydroxide at 60° to fifteen hours with sodium and potassium hydroxide at 50° . In all reactions a measurable amount of olefine was formed and in no case did the reaction go to completion. In an investigation of the hydrolysis of tertiary butyl bromide, McShan⁵ reports that tertiary butyl bromide was hydrolyzed completely by silver hydroxide at 60° in one

5. McShan, Thesis, University of Missouri, 1933.

hour, and by potassium hydroxide at 50° in two hours. He reported that silver hydroxide at 30° was the only hydrolytic agent which did not produce some olefine.

With secondary butyl bromide the temperature has a marked effect upon the rate of reaction; the hydrolysis going to apparent completion with silver hydroxide in three-fourths hours at 60° , one and one-half hours at 50° , and six hours at 30° , while with potassium hydroxide the reaction went to apparent completion in seven and one-half hours at 60° and fifteen hours at 50° . The time of reaction follows the law that the speed of reaction approximately doubles with each increase in temperature of 10° .

EXPERIMENTAL

Preparation of the Secondary Butyl Bromide

The secondary butyl bromide used in these reactions was synthesized by the action of gaseous hydrogen bromide on secondary butyl alcohol. The alcohol was the best grade obtainable from the Eastman Kodak Company and was redistilled through a 90 cm. fractionating column. It boiled at 98.9° . The hydrogen bromide generator consisted of a 250 cc. filter flask fitted with a mercury seal motor stirrer and a separatory funnel. About twenty grams of red phosphorus were placed in the flask and covered with 30 cc. of water. Bromine was added at the rate of about twenty drops each minute through the separatory funnel. The hydrogen bromide gas generated was passed through the side arm of the flask and through an inclined condenser which served to condense any water vapor. From the condenser the gas was purified by a train of tubes. The first of these tubes contained moist red phosphorus and fine asbestos which reacted with any bromine which came from the generator. The second tube contained anthracene and asbestos; this also served to remove any free bromine. The third tube contained anhydrous sodium sulphate which served to free the hydrogen

bromide of moisture. The gas was then passed through a trap, which was provided in case the alcohol should suck back, and then through a delivery tube into a flask containing 200 cc. of the secondary butyl alcohol. The alcohol was cooled with a salt-ice mixture. At the completion of the reaction the secondary butyl bromide and the aqueous hydrogen bromide separated into two layers. It required twenty-two hours for this reaction. The bromide layer was then separated and again saturated with hydrogen bromide. The secondary butyl bromide was washed with water, dilute sodium carbonate solution, and then with water until the washings gave a neutral test with litmus. It was then dried twenty-four hours over calcium chloride. After decanting from the calcium chloride, the bromide was fractionally distilled and the fraction boiling at $90.5 \pm .2^{\circ}$ at 740 mm. was collected for use in the reactions. The refractive index of the purified bromide was 1.4343 at 20° , compared to 1.4344 given in the literature⁶ for secondary butyl bromide.

The silver hydroxide used in the reactions was prepared by the action of silver nitrate and potassium hydroxide. A slight excess of silver nitrate was used

6. Int. Crit. Tab., I, p. 277.

so that no potassium hydroxide would remain in solution and then the silver hydroxide was washed free of the silver nitrate. Silver hydroxide is only slightly soluble in water and exists in the reaction mixture as Ag_2O (solid) $\xrightarrow{\text{H}_2\text{O}}$ AgOH (solution).

Hydrolysis with Silver Hydroxide

Reactions with silver hydroxide were carried out at temperatures of 30° , 50° , and 60° . The approximate time of the olefine formation was three-fourths hours at 60° , one and one-half hours at 50° , and six hours at 30° . The alcohol was not recovered.

The results for these tables are given in Table II.

Hydrolysis with Potassium Hydroxide

Reactions with potassium hydroxide were carried out at temperatures of 50° and 60° . The concentrations of potassium hydroxide were 2%, 5.6% (1.069 N.), and 25%. The approximate time of olefine formation for the 2% and the 5.6% was seven and one-half hours at 60° and fifteen hours at 50° , while that of the 25% solution was eleven hours at 60° . The reaction mixtures were worked up as follows. A small amount of solid phenolphthalein was added to each reaction mixture. The mixture was

then neutralized, using dilute nitric acid. About 100 cc. of the neutral mixture were then distilled off. The distillation was carried out using a 90 x 2 cm. pyrex fractionating column containing 75 cm. of cut pyrex glass rings. The column was sealed directly to a spiral condensing system which was immersed in a water-ice mixture. The rate of distillation was about sixty drops per minute. The distillate was collected in a small flask surrounded by ice.

In order to determine if any hydrolysis took place on distillation of the neutral mixture, 12 grams of the secondary butyl bromide were placed in 1000 cc. of halogen free water and about 100 cc. of the mixture were distilled. Neither the distillate nor the residue in the distillation flask gave a test for halide with silver nitrate solution, indicating that no hydrolysis had taken place.

The olefine was measured with a gas analysis apparatus, the olefine hydrocarbon being removed from the olefine-air mixture with fuming sulphuric acid and the volume of olefine determined by the loss of volume of the sample.

The results of the reactions are given in Table III.

Hydrolysis with Sodium Hydroxide

Reactions with sodium hydroxide were carried out with sodium hydroxide of 4.1% and 6% concentration, the temperature being 60° in all reactions. The time of olefine formation was about seven hours, or about the same as that of the potassium hydroxide reactions at 60° . The 4.1% solution had the same normality as that of the 5.6% potassium hydroxide solution, that of 1.069 N. The purpose of this was to establish a relationship between their respective actions when the same number of molecules of the hydrolytic agent were present. The average mole ratio of olefine to alcohol produced by the 1.069 N. potassium hydroxide was .64086, while that of the 1.069 N. sodium hydroxide was .53463. The alcohol was recovered as described above.

The results of these reactions with sodium hydroxide are given in Table IV.

Hydrolysis with Calcium Hydroxide

These reactions were carried out using an aqueous suspension of the reagent, so that the solutions were saturated at all times. The approximate reaction time was seven and one-half hours at 60° . Before distillation of the alcohol the solution was made acid with nitric

acid so as to dissolve all the excess calcium hydroxide and then brought back to neutrality with potassium hydroxide solution.

The results of these reactions are shown in Table V.

Hydrolysis with Barium Hydroxide

The reactions were conducted in the same manner as those of the calcium hydroxide. Aqueous suspensions of the reagent were used at 60°. The time of olefine formation was again about seven hours. Before distillation of the alcohol it was again necessary to make the reaction mixture acid with dilute nitric acid and then come back to neutrality with potassium hydroxide.

The results of these reactions are shown in Table VI.

A summary of all the reactions are given in Table VII.

Table I

Data for the Refractive Index - Concentration Graph

per cent alcohol	refractive index
1.56	1.3340
3.67	1.3362
5.04	1.3375
5.83	1.3387
9.92	1.3431
9.98	1.3430
12.49	1.3460
14.97	1.3480
65.29	1.3815
67.01	1.3823
71.01	1.3842
71.07	1.3833*
73.96	1.3858
75.84	1.3865
77.88	1.3877
79.90	1.3883
82.20	1.3893
85.72	1.3905
90.27	1.3922
94.41	1.3936
96.19	1.3940
100.00	1.3950

* Irregularity probably due to experimental error.

Table II

Hydrolysis with Silver Hydroxide

	I 60°	II 60°	III 60°	IV 50°
Volume olefine	424.3	405.8	428.1	403.6
Weight olefine	1.0607	1.0145	1.0703	1.0090
Total weight silver bromide	11.8784	11.5700	11.4609	11.3375
Weight silver bromide equivalent to olefine	3.5532	3.3988	3.5857	3.3801
Weight silver bromide equivalent to alcohol	8.3252	8.1712	7.8752	7.9574
Weight sec-butyl alcohol	3.2839	3.2233	3.1065	3.1389
Moles olefine	.01892	.018098	.019093	.017999
Moles sec-butyl alcohol	.04433	.043511	.041934	.042376
Moles olefine/moles alcohol	.42682	.41593	.45530	.42479
	V 50°	VI 30°	VII 30°	
Volume olefine	407.3	423.3	278.4	
Weight olefine	1.0182	1.0582	0.6960	
Total weight silver bromide	11.4662	11.6125	8.2389	
Weight silver bromide equivalent to olefine	3.4110	3.5455	2.3314	
Weight silver bromide equivalent to alcohol	8.0552	8.0670	5.9075	
Weight sec-butyl alcohol	3.1775	3.1985	2.4487	
Moles olefine	.018163	.018880	.012414	
Moles sec-butyl alcohol	.042892	.042956	.037594	
Moles olefine/moles alcohol	.42346	.43952	.39464	

17

Note: All volumes are in cubic centimeters, all weights in grams.

Table III

Hydrolysis with Potassium Hydroxide

	I 2% 60°	II 2% 50°	III 25% 60°	IV 25% 60°
Volume olefine	386.2	299.2	590.3	531.3
Weight olefine	0.9671	0.7480	1.4758	1.3258
Total weight potassium bromide	8.5092	7.3405	6.5645	5.9866
Weight potassium bromide equivalent to olefine	2.0531	1.6161	3.1330	2.8196
Weight potassium bromide equivalent to alcohol	6.4561	5.7244	3.4315	3.1670
Weight sec-butyl alcohol	4.0187	3.5631	2.1360	1.9713
Moles olefine	.017252	.013343	.026235	.023691
Moles sec-butyl alcohol	.054248	.048100	.028833	.026611
Moles olefine/moles alcohol	.31802	.27740	.91302	.89021
	V 5.6% 60°	VI 5.6% 60°	VII 5.6% 50°	VIII 5.6% 50°
Volume olefine	654.9	656.7	564.6	545.8
Weight olefine	1.6372	1.6418	1.4115	1.3644
Total weight potassium bromide	8.7260	9.0235	7.7120	7.4466
Weight potassium bromide equivalent to olefine	3.4757	3.4856	2.9965	2.8965
Weight potassium bromide equivalent to alcohol	5.2503	5.5379	4.7155	4.5501
Weight sec-butyl alcohol	3.2681	3.4471	2.9352	2.8328
Moles olefine	.029205	.029288	.025178	.024328
Moles sec-butyl alcohol	.044116	.046533	.039622	.038233
Moles olefine/moles alcohol	.66199	.62940	.63546	.63658

18

Note: All volumes are in cubic centimeters, weights in grams.

Table IV
Hydrolysis with Sodium Hydroxide

	I 4.1%	II 4.1%
Volume olefine		
Weight olefine	611.7	577.6
Total weight sodium bromide	1.5235	1.4440
Weight sodium bromide equivalent to olefine	8.0253	7.6396
Weight sodium bromide equivalent to alcohol	2.8071	2.6507
Weight sec-butyl alcohol	5.2182	4.9889
Moles olefine	3.7562	3.5911
Moles sec-butyl alcohol	.027278	.025756
Moles olefine/moles alcohol	.050706	.048478
	.53795	.53131
	III 6%	IV 6%
Volume olefine		
Weight olefine	665.5	656.7
Total weight sodium bromide	1.6637	1.6418
Weight sodium bromide equivalent to olefine	8.3155	8.0582
Weight sodium bromide equivalent to alcohol	3.0542	3.0139
Weight sec-butyl alcohol	5.2613	5.0443
Moles olefine	3.7873	3.6311
Moles sec-butyl alcohol	.029677	.029287
Moles olefine/moles alcohol	.051124	.049059
	.58051	.59747

Note: All volumes are in cubic centimeters, all weights in grams.

Table V

Hydrolysis with Calcium Hydroxide

	I	II
Volume olefine	245.2	207.7
Weight olefine	0.6130	0.51925
Total weight calcium bromide	7.9028	6.8691
Weight calcium bromide equivalent to olefine	1.0928	0.9256
Weight calcium bromide equivalent to alcohol	6.8100	5.9435
Weight sec-butyl alcohol	5.0474	4.4051
Moles olefine	.010934	.009260
Moles sec-butyl alcohol	.068134	.059460
Moles olefine/moles alcohol	.16047	.15572

Table VI

Hydrolysis with Barium Hydroxide

	I	II
Volume olefine	359.5	390.9
Weight olefine	0.9267	0.9772
Total weight barium bromide	9.6239	9.9642
Weight barium bromide equivalent to olefine	2.3823	2.5907
Weight barium bromide equivalent to alcohol	7.1671	7.3735
Weight alcohol	3.5730	3.6757
Moles olefine	.016533	.017434
Moles sec-butyl alcohol	.048231	.048920
Moles olefine/moles alcohol	.34269	.35136

Note: All volumes are in cubic centimeters, all weights in grams.

Table VII

Summary of the Reactions

Hydrolytic agent	Temperature	Time of Olefine Formation	Time reaction was run	Mole Ratio Olefine Alcohol
AgOH	60°	3/4 hours	2 hours	.42682
AgOH	60°	3/4	2	.41593
AgOH	60°	3/4	2	.45530
AgOH	50°	1 1/2	4	.42479
AgOH	50°	1 1/2	4	.42346
AgOH	30°	6	8	.43952
AgOH	30°	6	8	.39464
KOH 2%	60°	7 1/2	8 1/2	.31802
KOH 2%	50°	15	16	.27740
KOH 5.6%	60°	7 1/2	8 1/2	.66199
KOH 5.6%	60°	7 1/2	8 1/2	.62940
KOH 5.6%	50°	15	16	.63546
KOH 5.6%	50°	15	16	.63658
KOH 25%	60°	11	12	.91302
KOH 25%	60°	11	12	.89021
NaOH 6%	60°	7	8	.58051
NaOH 6%	60°	7	8	.59747
NaOH 4.1%	60°	7	8	.53795
NaOH 4.1%	60°	7	8	.53131
Ca(OH) ₂	60°	7 1/2	8 1/2	.16047
Ca(OH) ₂	60°	7 1/2	8 1/2	.15572
Ba(OH) ₂	60°	7	8	.34269
Ba(OH) ₂	60°	7	8	.35136

SUMMARY

1. Secondary butyl bromide was synthesized by passing gaseous hydrogen bromide into secondary butyl alcohol.
2. The reactions between secondary butyl bromide and the hydroxides of silver, potassium, sodium, calcium, and barium were investigated. In all cases, hydrolysis was accompanied by olefine formation.
3. The formation of olefine seems to be related to the concentration of the hydrolytic agent, while the temperature has little effect, except on the speed of reaction.

BIBLIOGRAPHY

- Conant, J. B., Kirner, W. R., and Hussey, R. E., The Relation Between the Structure of Organic Halides and the Speeds of Their Reaction with Inorganic Iodides, Journal of the American Chemical Society, 47, p. 488 (1925).
- McShan, William Hartford, Hydrolysis of Tertiary Butyl Bromide, Thesis, University of Missouri, 1933.
- Nicolet, B. H., and Stevens, D. R., The Alcoholysis and Hydrolysis of Some Alkyl Halides in Neutral Solution, Journal of the American Society, 50, p. 135 (1928).
- Noller, C. R., and Dinsmore, R., The Reaction of Alkyl Bromides with Pyridine, Journal of the American Chemical Society, 54, p. 1025 (1932).
- Slator, Arthur, The Chemical Dynamics of the Reactions Between Sodium Thiosulphate and Organic Halogen Compounds, Journal of the Chemical Society, 95, p. 93 (1909).
- Washburn, Edward W., and others, International Critical Tables, 1, p. 277. Published for the National Research Council by McGraw-Hill Book Co., Inc. New York (1928).

ACKNOWLEDGEMENT

I wish to express my sincerest thanks to Dr. H. E. French, Associate Professor of Organic Chemistry at the University of Missouri, who suggested this problem, and whose valuable assistance and cooperation, made possible its completion.

Walter W. Jöhler

Chemistry Laboratory
University of Missouri
Columbia

UNIVERSITY OF MISSOURI
COLUMBIA

SCHOOL OF AGRICULTURE
DEPARTMENT OF SOILS

July 20, 1933

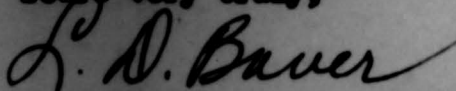
Dean W. J. Robbins

Graduate School

Dear Dean Robbins:

I have read the thesis of Walter William
Johler and find that it meets the general standard
which has been established in this institution for the
Master's dissertation.

Yours very truly,




L. D. Bauer

Assistant Professor

Film
Neg.
Reel 73
T 749-759

M.A. THESIS
JOHANN - JOHNSON

University of Missouri - Columbia



010-103734069

G
N. Y.