

THE REACTION OF SODIUM BOROXYDRIDE
WITH BENZOIC ACID

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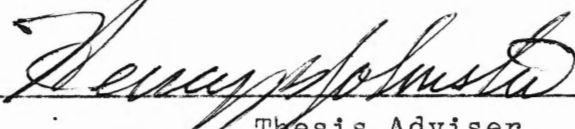
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INTRODUCTION

Sodium borohydride as well as sodium trimethoxy borohydride are of special interest because of their potential usefulness as reducing agents and as sources for the generation of hydrogen. Uranium borohydride and its derivatives are of interest because they are the most volatile compounds of uranium except the hexafluorides (12).

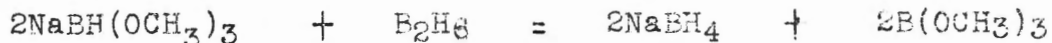
Previous studies of sodium borohydride, NaBH_4 , as a reducing agent by Schlesinger, Schaeffer and collaborators have been concerned with the application in the fields of inorganic and analytical chemistry, but they have nevertheless served to indicate the potential value of sodium borohydride in organic synthesis. Dr. Saul Chaiken and Dr. W. G. Brown were the first two to use sodium borohydride as a reducing agent with organic compounds. They successfully reduced aldehydes and ketones to their corresponding alcohols (5).

The purpose of the research done for this thesis is to investigate the reducing power of sodium borohydride with benzoic acid in the absence of solvents.

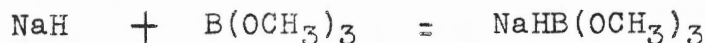
HISTORICAL

Synthesis of Sodium Borohydride

Sodium borohydride, NaBH_4 , was first synthesized and identified by Schlesinger and Brown (14, 15, 16) from sodium trimethoxy borohydride and diborane.

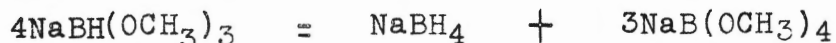


Sodium trimethoxy borohydride was prepared from sodium hydride, NaH , and methyl borate, $\text{B}(\text{OCH}_3)_3$ (12).

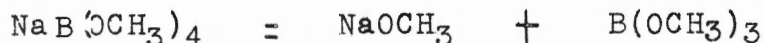


This exothermic reaction proceeds with moderate rapidity and with a great increase in the quantity of the product. It may be carried out in the absence of any liquid medium other than methyl borate itself.

At high temperature sodium trimethoxy borohydride breaks down as follows (4):

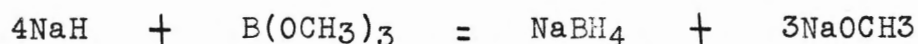


Continued heating with constant evacuation causes the decomposition of sodium tetramethoxy borate, $\text{NaB}(\text{OCH}_3)_4$, to sodium methoxide, NaOCH_3 , and trimethyl borate, $\text{B}(\text{OCH}_3)_3$.

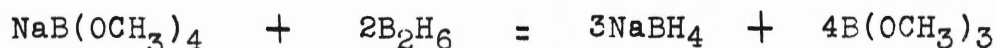


The residual NaOCH_3 and NaBH_4 are separated by the use of isopropyl amine or ammonia, which dissolves sodium borohydride but not sodium methoxide (8, 13).

Sodium hydride, NaH , reacts with trimethyl borate, $\text{B}(\text{OCH}_3)_3$, or triethyl borate, $\text{B}(\text{OC}_2\text{H}_5)_3$, without any solvent to give sodium borohydride (9, 13).



It was also observed that sodium tetramethyl borate reacted with diborane yielding sodium borohydride (9, 17).



The borohydride may also be obtained by heating a mixture of sodium hydride and boric oxide, B_2O_3 , in a glass vessel at $300^\circ\text{-}350^\circ\text{C}$ (13).

Physical Properties of Sodium Borohydride

Sodium borohydride is a white crystalline salt. It is thermally stable. Heated in an evacuated tube, it exhibits no apparent change at temperatures approaching 400°C (17, 23). By means of an X-ray powder method it has been shown that the crystal structure of sodium borohydride is based upon a face centered cubic lattice with the unit cell containing four Na and four B atoms.

It is very soluble in liquid ammonia and in the lower aliphatic amines. It is also soluble in water. It is insoluble in dioxane, ethyl acetate, ethyl ether, diethyl amine, and trimethyl amine (9,1).

Tables of solubility and thermodynamic data are given in the following pages.

TABLE I
 SOLUBILITY OF SODIUM BOROHYDRIDE
 IN SEVERAL SOLVENTS (18)

Solvent	B.P. °C	°C	Solubility
			Grams/100 Grams Solvent:
Liquid Ammonia	-33.3	25	104
Methyl Amine	- 6.5	-20	27.6
Ethyl amine	16.6	17	20.9
N-Propyl Amine	48.7	28	9.6
Isopropyl Amine	34.0	28	6.0
N-Butyl Amine	77.8	28	4.9
Ethylene Diamine	118.0	75	22.0
Cyclohexyl Amine	134.0	28	1.8
Aniline	184.0	75	0.6
Pyridine	115.3	25	3.1
Pyridine	115.3	75	3.4
Morpholine	128.3	25	1.4
Morpholine	128.3	75	2.5
Acetonitrile	82.0	28	0.9

TABLE II
THERMODYNAMIC PROPERTIES OF NaBH_4 AT 25°C

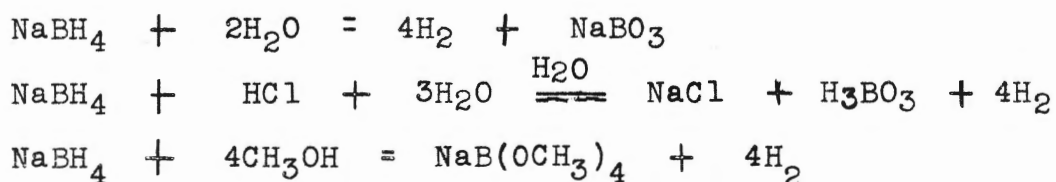
Entropy	=	25,024 cal./mole-deg.	(3)
Entropy of formation	=	51.58 cal./mole-deg.	(3)
Heat of formation	=	-43.83 ± 0.07 kcal./mole	(7)
Free energy of formation	=	-28.45 kcal/mole	(3)
Internal energy of hydrolysis	=	-66,760 cal./mole	(2)
Heat of hydrolysis	=	-57.0 kcal./mole	(13)
Density	=	1.08 g./ml.	(7)
Specific heat	=	0.55 ± 0.1 cal./g. deg.	(7)
Heat of solution (0.07 molal) in isopropyl amine	=	-7.6 kcal./mole	(13)
Heat of solution (1 molal) in ammonia	=	-10 kcal./mole	(13)

Chemical Properties and Reactions.

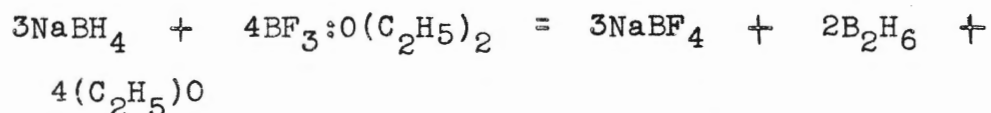
Hydrolysis of sodium borohydride in cold water is very slow. Moderately concentrated aqueous solutions at room temperature lose about 10% of their available hydrogen per day and the reaction becomes slower with increasing time. At 100°C, sodium borohydride completely reduces water in one or two minutes, a fact that is advantageous when the compound is used as a reducing agent in analytical procedures. (12)

Reduction can also be greatly catalyzed by small quantities of metal salts. Cobaltous salts are the most effective catalysts. (18) Their reaction has been shown to be due to formation of a compound Co_2B , which is the actual catalyst (9, 13).

Sodium borohydride reacts with dilute hydrochloric acid and methanol (18).



The reaction with methanol proceeds at an appreciable rate at -40°C. Sodium borohydride reacts quantitatively with boron fluoride etherate to liberate diborane (18).

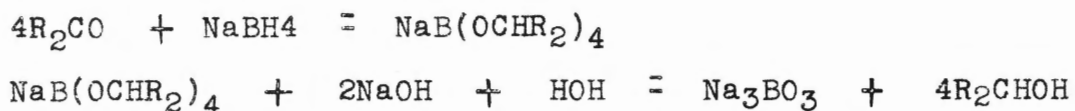


Since sodium borohydride is a very powerful reducing agent, its reactions can be divided into (1) reactions with inorganic compounds and (2) reactions with organic compounds.

Sodium borohydride in aqueous solution reduces Iron (III) to Iron (II). Thallium (III) in alkaline solution is reduced

to Thallium (I). Vanadium (V) as a sulfate is reduced in acid media to Vanadium (IV). Silver iodide in acid solution is quantitatively reduced to silver. Manganese (VII) yields Manganese (II), Manganese (IV) and Manganese (VI) in acid, neutral and basic solutions. In acid and neutral solutions, Chromium (VI) is reduced to Chromium (III), but no reduction occurs in alkaline solution. Molybdenum (VI) is reduced to Molybdenum (V) in acid or neutral solution (11).

Sodium borohydride in water or methanol solution is an effective reagent for the conversion of aldehydes or ketones to the corresponding alcohols. The reactions occur rapidly at room temperature in most cases, although occasionally heating is required. Reduction of aliphatic aldehydes is carried out in an aqueous solution of sodium borohydride; hydrolysis of the intermediate boron ester takes place concurrently. In the reduction of aromatic aldehydes and some of the ketones studied, subsequent heating with alkali was necessary in order to liberate the alcohols. By means of quantitative observations, it has been shown that four moles of aldehyde or ketone reacted with one mole of the borohydride and the course of the reactions may be formulated as follows: (5)



Acid chlorides are reduced to primary alcohols in non aqueous media. Reaction is vigorous with aliphatic acid chlorides, but aromatic acid chlorides require heating (5).

Reduction of the enol acetate of cholestenone by sodium borohydride in methanoic acid solution yielded approximately

75% cholesterol. Reduction with lithium aluminium hydride, using anhydrous ether as the solvent with reaction carried out in an atmosphere of nitrogen, gave a yield of 35% cholesterol (6).

Sodium borohydride is an excellent reagent for converting carbohydrates with a reducing group into the corresponding alcohols (24).

Sodium borohydride has been employed in aqueous solution to effect the following reductions: D-lyxono-r-lactone to D-lyxose (or D-arabitol) D-glucuronate and D-galacturonate salts to L-gulono-r-lactone, respectively; methyl (methyl-D-galactopyranosid)-uronate(1), it's B-D-anomer and methyl (methyl-D-glucopy ranosid)-uronate to the methyl pyranosides of α -D-galactose(2), B-D-galactose and α -D-glucose, respectively (24,1).

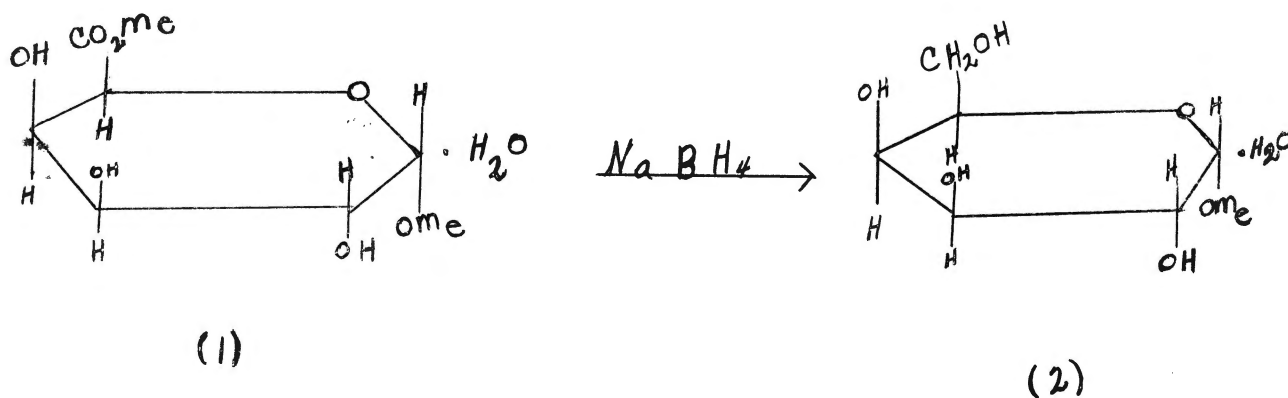


TABLE III
REDUCTION OF ALDEHYDES AND KETONES
IN AQUEOUS SOLUTIONS (5)

Compound	Product	% Yield
Acetonylacetone	Hexanediol-2-5	88
N-Butyraldehyde	N-Butanol	85
Chloral Hydrate	2,2,2-trichloroethanol	61
Crotonaldehyde	Crotyl Alcohol	85
Cyclopentanone	Cyclopentanol	90
Diacetyl	Butanediol-2-3	62
Levulinic Acid	r-Valerolactone	81
Mesityl Oxide	4-Methyl-3-pentenol	77
Methyl Ethyl Ketone	s-Butanol	87

TABLE IV
REDUCTION OF ALDEHYDES AND KETONES
IN METHANOL SOLUTIONS (5)

Compound	Product	% Yield
Anisaldehyde	Anisyl alcohol	96
Benzil	Hydrobenzoin	89
w-Bromoacetophenone	Styrene bromohydrin	71
Cinnamaldehyde	Cinnamyl alcohol	97
Dicyclohexyl ketone	Dicyclohexyl carbinol	88
p-Dimethylamino- benzaldehyde	p-Dimethylamino- benzyl alcohol	96
m-Hydroxybenzaldehyde	m-Hydroxybenzyl alcohol	93
m-Nitrobenzaldehyde	m-Nitrobenzyl alcohol	82

TABLE V
REDUCTION OF ACID CHLORIDES (5)

Compound	Product	% Yield
Benzoyl chloride	Benzyl alcohol	76
n-Butyoyl chloride	n-Butanol	81
Cinnamoyl chloride	Hydrocinnamyl alcohol	12
Monoethyl succinate acid chloride	Butyrolactone	40
Palmitoyl chloride	Cetyl alcohol	87
O-Phthayl chloride	Phthalide	49
	Phthalyl alcohol	15

TABLE VI
REDUCTION OF SUGARS WITH
SODIUM BOROHYDRIDE (24)

Sugar	Acetylated Product	% Yield
D-Glucose	Sorbitol hexaacetate	78
D-Mannose	D-Mannitol hexaacetate	92
D-Galactose	Dulcitol hexaacetate	87
L-Arabinose	L-Arabitol pentaacetate	87.5
D-Xylose	Xylitol pentaacetate	80
D-Fructose	A mixture of sorbitol and D-Mannitol Hexaacetate	75
Maltose	Maltitol nonaacetate	70

EXPERIMENTAL

Purification of Sodium Borohydride

Crude sodium borohydride (20 grams, 0.5262 mole) and 500 ml. of anhydrous pyridine were mixed and the solution was allowed to stand for six hours with occasional shaking. At the end of the sixth hour, the sodium borohydride-pyridine solution was filtered by suction using a fine fritted glass funnel. The residue was washed with another 200 ml. of anhydrous pyridine. The sodium borohydride was precipitated by adding anhydrous diethyl ether until no more precipitate separated. The sodium borohydride was collected by suction using a Buchner funnel. It was then placed in a drying pistol and dried at 100°C for five hours, using a water aspirator with drying tubes to obtain a partial vacuum. During the five hours of heating, the pistol was occasionally opened to remove any pyridine which condensed at the cold end of the apparatus. After drying was completed, the pistol was removed to a dry box. The pure sodium borohydride was ground in a mortar into a very fine powder. It was then placed in weighing bottles which were stored in a desiccator.

Reaction of Sodium Borohydride and Acetic Acid

Sodium borohydride is a powerful reducing agent. Very vigorous reactions occur when liquid organic acids react with sodium borohydride. To prevent such an instantaneous reaction, the glacial acetic acid was cooled down to its

freezing point. Nitrogen gas then flushed through the reaction flask before and after the addition of sodium borohydride. Yet, with all these precautions explosions occurred, because of the presence of oxygen. Two runs were performed without any results. Hence, it was then decided to substitute benzoic acid in place of the glacial acetic acid.

Reaction of Sodium Borohydride and Benzoic Acid

In these experiments, sodium borohydride was weighed in a dry box then placed in the reacting vessel. At times during the course of the experiments, the benzoic acid weighed on an ordinary balance, then transferred into the reacting vessel already containing the borohydride in an atmosphere of Nitrogen gas.

The Effect of Heat Upon Reaction

Sodium borohydride (0.5929 grams, 0.0156 mole) and benzoic acid (3.9223 grams, 0.0321 mole) were thoroughly mixed in a three neck, round bottle flask in an atmosphere of nitrogen, connected to the apparatus and then the flask was immersed in a wax bath. The temperature was raised slowly to 200°C without noticeable change in color. At temperatures around 129°C-138°C maximum reaction was noted with vigorous evolution of hydrogen gas which continued for three minutes. The volume of hydrogen gas collected was 785 ml. at a room temperature of 29.53°C and at a room pressure of 744.58 mm. Hg.

At the end of the reaction, the solid residue from the reaction was collected in a 600 cc beaker. Two ether extrac-

tions of 100 cc each were carried out in order to separate unreacted benzoic acid along with benzyl alcohol which might have formed during the reaction from the bulk of the material. The ether soluble product was transferred into a distilling flask and the ether distilled. The residue melted at 122°C which was the melting point of benzoic acid.

To the ether insoluble material was added 50 cc of approximately 0.5 N NaOH, and refluxed for one hour at a temperature of 100°C. At the end of the refluxing, another ether extraction was carried out. The ether soluble portion was transferred into a 500 cc flask and the ether distilled. The residue was in too small an amount to analyze.

The amount of sodium borohydride and benzoic acid in gas measurement was found to be vital during the course of the experiment because of the small size of the gas measuring burette. Hence five runs were made to determine the best mole ratio.

Run I - Sodium borohydride (0.2069 grams, 0.0054 mole) and benzoic acid (1.3555 grams, 0.0229 mole) were thoroughly mixed in a three neck, round, standard taper flask in an atmosphere of nitrogen, and then immersed in a water bath. At a temperature of 129°C-123°C the reaction reached its maximum. The volume of hydrogen gas collected was 160 cc or 0.0064 mole, at a room pressure of 746.58 mm Hg. and a room temperature of 26.3°C.

Run II - Sodium borohydride (1.6140 grams, 0.0425 mole) and benzoic acid (10.3619 grams, 0.1727 mole) were reacted. At

128°C reaction started with fuming inside the flask. As the temperature kept increasing up to 133°C the amount of hydrogen gas evolved was more than the gas measuring burette could hold; therefore, the three neck, standard taper flask was opened to release the excess gas. This run was without significance.

Run III - Sodium borohydride (0.4928 grams, 0.131 mole) and benzoic acid (4.8021 grams, 0.8000 mole) were reacted. Gas evolution started at 128°C and proceeded up to 142°C, then it diminished slowly. Temperature was raised to 195°C. The volume of hydrogen gas collected was 445 ml. or 0.0176 mole at a room temperature of 26.2°C and at a room pressure of 739.80 mm. Hg.

Run IV - Sodium borohydride (0.5047 grams, 0.0132 mole) and benzoic acid (4.7253 grams, 0.0787 mole) were reacted. Reaction commenced at 127°C and became vigorous as the temperature kept increasing to 145°C, and then slowly receded. The volume of hydrogen gas collected was 315 ml. or 0.125 mole at a room temperature of 26.1°C and at a room pressure of 751.80 mm. Hg.

Run V - Sodium borohydride (0.2064 grams, 0.0054 mole) and benzoic acid (1.6666 grams, 0.0278 mole) were reacted. The volume of hydrogen gas collected was 180 ml. or 0.0072 mole at a room temperature of 26.0°C and a room pressure of 750.00 mm. Hg.

TABLE VII
 THE EFFECT OF VARYING THE MOLE RATIO
 OF THE REACTANTS

Run number	I	II	III	IV	V
Moles of NaBH_4	0.0054	0.0425	0.0131	0.0132	0.0054
Moles of $\text{C}_6\text{H}_5\text{COOH}$	0.0229	0.1727	0.8000	0.0787	0.0278
Mole ratio of reactants	4.2407	4.0635	6.1069	5.9621	5.1481
Moles gas evolved	0.0064	_____	0.0176	0.0125	0.0072
Moles gas per mole borohydride	1.1851	_____	1.3435	0.9469	1.3333

Although reaction between sodium borohydride and benzoic acid was initiated around 128°C , yet the reaction never went to completion. In these experiments one should bear in mind the difference in the melting points of sodium borohydride and benzoic acid, which was a great obstacle in their reaction.

In order to be able to arrive at a final product, a series of runs were carried out, using different mole ratios each run, and neglecting the volume of hydrogen gas given off.

Run I - Sodium borohydride (2.0000 grams, 0.0526 mole) and benzoic acid (12.8021 grams, 0.1049 mole) were mixed in a 500 cc three-neck flask in a nitrogen atmosphere. The flask was then dipped in a water bath and heat applied slowly. Reaction started around 128°C . At the end of the reaction three portions of 200 cc anhydrous diethyl ether were used for the extraction. The ether insoluble portion was hydrolyzed with 200 cc of approximately 0.5 N NaOH solution for one hour. At the end of hydrolysis another ether extraction was made. The residual ether was distilled. Nothing remained in the distilling flask. The sodium hydroxide solution was retained.

Run II - The same amount of reactants as were Run I was used. The ether insoluble product was divided into two portions. The first portion was hydrolyzed with 200 cc of approximately 0.5 N NaOH solution. The second portion was washed with cold distilled water of about 4°C . Sodium borohydride is water soluble. During the washing with cold distilled water about one-fourth of the reactant went into solution with foam formation. The insoluble residue was collected and dried. This white product

was ground and a melting point was taken. At 434°C it started turning gray, without melting. Due to the decomposition of the material at such a high temperature, the melting point determination was stopped.

The hydrolyzed portion was extracted with diethyl ether and the ether was distilled. The residue had a smell characteristic of either benzyl alcohol or benzaldehyde. The residue was in too small an amount to analyze.

Run III - Sodium borohydride (4.2160 grams, 0.1109 mole) and benzoic acid (40.6069 grams, 0.3324 mole) were mixed and heated to 248°C . As the temperature was increased, the reaction became vigorous. After the reaction subsided, three ether extractions were carried out. The ether insoluble product was hydrolyzed with 200 cc of approximately 0.5 N NaOH solution for one hour. After the ether was distilled, the residue was found to be yellow in color and about three-fourth of a cc. Odor of the residue was very close to that of benzaldehyde. A Beckmann DU Spectrophotometer was used to determine the type of curve. Cyclohexane was used as the solvent. A similar run, using pure and known benzaldehyde was made. The two curves obtained were different. This test, so far, explained the absence of benzaldehyde.

Run IV - Sodium borohydride (2.2698 grams, 0.0598 mole) and benzoic acid (14.5278 grams, 0.1107 mole) were placed in a three neck reaction flask; then nitrogen gas was passed through for fifteen minutes. At 128°C the benzoic acid began melting with the evolution of a gas continuing up to 145°C . Ether extrac-

tion was carried out on the residue; using three extractions of 200 ml. each. The ether soluble portion was transferred into a distilling flask and the ether distilled from the residual benzoic acid. The insoluble portion was refluxed for one and one-half hours with 2000 cc of approximately 0.5 N NaOH solution. At the end of the one and one-half hours, the solution was extracted with another three portions of 200 cc ether. The ether soluble part was put into a distilling flask and the ether distilled. The yellow colored residue consisted of a mixture of benzoic acid and either benzaldehyde or benzyl alcohol.

The following test was run for the detection of the carbonyl radical, that is, detection of benzaldehyde: fifteen milliliters of hydroxylamine hydrochloride reagent and 50 ml. of pyridine-bromophenol blue solution were put in a 250 ml. glass-stoppered Erlenmeyer flask, fitted with a reflux condenser. To the solution was added 0.23 cc of the unknown material. The resulting mixture was refluxed for two hours. At the end of the two hours the solution was cooled to within 5°C of room temperature and then titrated with 0.5 N sodium hydroxide in 90% methanol.

$$\% \text{ carbonyl compound} = \frac{\text{milliliters NaOH} \times \text{N NaOH} \times \text{mol.wt. comp.} \times 100}{\text{grams sample} \times 10000}$$

About 4.5 cc sodium hydroxide was used without change in color. More of the 0.5 N NaOH solution was added and still no change in color resulted, which meant that the compound was not benzaldehyde. If it were benzaldehyde a definite change in color should occur and percentage of the carbonyl should have been

101.6 \pm 1.4 % (21).

Tollen's Test - When the unknown compound was added to Tollen's reagent in a test tube nothing happened. Upon heating, a dark brown precipitate was formed. No silver mirror formation was observed on the side of the test tube. When known benzaldehyde was substituted, a silver mirror formation was distinctively observed on the sides of the test tube. Again the test for benzaldehyde was negative.

Benzidine Test - With known benzaldehyde and some benzidine in a test tube, the following changes in color were observed: yellow to red to yellow precipitate. With a sample of the unknown, the color was yellow. When heat was applied, no precipitate was formed and the color remained yellow. Once more, this constituted a negative test for the presence of benzaldehyde.

Since tests for benzaldehyde had proved negative, it was decided to run some experiments for testing for the presence of benzyl alcohol.

Run I - Sodium borohydride (2.7569 grams, 0.0725 mole) and benzoic acid (26.4752 grams, 0.2171 mole) were reacted. The benzoic acid inside the flask started melting with hydrogen gas evolving at a temperature of 128°C. Temperature was increased up to 240°C with no change in color of the reactants. The ether insoluble portion was refluxed with 200 cc of approximately 0.5 N hydrochloric acid, instead of sodium hydroxide. This substitution was made, for fear that, during the refluxing with sodium hydroxide solution, a Cannizaro Reaction might have taken place. Heat was applied for one hour at 100°C.

At the end of the heating period, the solution was cooled. It was observed during the cooling process that three layers formed. In the upper layer was benzoic acid; the second layer was pale yellow in color, though solid; and the third layer was liquid, mostly the hydrochloric acid solution. The hydrochloric acid solution was separated, and extracted with ether. When the ether was distilled, white crystals were formed. These were identified as benzoic acid. The second layer, a pale yellow solid, was dissolved in ether. The ether portion was distilled. Near the end of the ether distillation, the pale yellow solution suddenly foamed into a semisolid mass. The melting point of the solid material was the same as that of benzoic acid.

Run II - Sodium borohydride (4.2819 grams, 0.1126 mole) and benzoic acid (68.6140 grams, 0.5624 mole) were reacted. The ether insoluble material was refluxed with 200 cc of approximately 0.5 N sodium hydroxide at 100°C for one and one half hours. At the end of hydrolysis, the solution was extracted with 200 cc of ether. The ether soluble portion, which was yellow in color, was transferred to a distilling flask, and the ether distilled. A very small amount of a pale yellow liquid remained in the distilling flask. The odor was characteristic of benzyl alcohol. Xanthate test for the presence of alcohol proved positive.

Run III - Sodium borohydride (3.5701, 0.0939 mole) and benzoic acid (37.1529 grams, 0.3045 mole) were mixed. Gas evolution commenced at 133°C, became rapid at 135°C. An ether extraction

was performed in three portions of 200 cc each, and the ether distilled. The residue was hydrolyzed with approximately 1 N sodium hydroxide solution for four hours. A final ether extraction was made and the ether distilled, leaving a yellow residue of about one milliliter. The odor was similar to that of benzyl alcohol. The preparation of an alcohol derivative of the unknown compound was attempted. A urethan derivative was made, using the following procedure: 0.5 cc phenyl isocyanate was mixed with the unknown compound in a test tube, heated in a water bath for five minutes and then transferred into a flask full of ice. The solid material formed was purified by means of carbon tetrachloride, heated in a water bath and filtered. The filtrate was transferred into a 50 cc beaker and immersed in an ice bath. A precipitate began forming. The precipitate was collected and dried. It melted around 176° - 177° C. In the literature the melting point of benzyl phenyl urethane was given as 177° - 178° C. This benzyl phenyl urethan derivative served as a definite positive test for the presence of benzyl alcohol.

Run IV - Sodium borohydride (2.4931 grams, 0.0656 mole) and benzoic acid (23.9238 grams, 0.1960 mole) were reacted. Reaction started around 124° C and proceeded vigorously up to 128° C. From 129° - 146° C reaction was slow. At the end of the reaction, extractions, using 150 cc of ether, each were carried out. The ether insoluble solution was put into a flask and retained. The ether soluble part was transferred into a distilling flask and distilled, leaving approximately one milliliter of a yellow liquid as residue. Tests proved that once again the residue was benzyl alcohol.

Run V - Same mole ratio as run IV was used, that is 2.4931 grams sodium borohydride to 23.9238 grams benzoic acid. The reactants were put in a 250 milliter three-neck round bottom flask. Nitrogen gas was flushed through for fifteen minutes. Gas evolution which commenced at 128°C became rapid as the temperature increased to 132°C. The ether insoluble material was refluxed for three and one half hours with 200 cc of approximately 0.5 N sodium hydroxide solution. The solution was cooled and then another three ether extractions were performed, again using 200 cc of ether for each. The ether soluble portion was transferred into a distilling flask and the ether distilled, leaving some yellow liquid as residue. By means of a Beckmann DU Spectrophotometer an ultra-violet light spectrum was determined for the residue for comparison with spectrum of an unknown concentration of benzyl alcohol. The two obtained curves were very similar. Cyclohexane was used as the solvent. This run verified that benzyl alcohol was the final product obtained by the reduction of benzoic acid with sodium borohydride.

Formation of Sodium Tetraborate

During the course of the experiments, the sodium hydroxide solutions after the ether extractions were retained in flasks. These flasks were not numbered according to their runs. About three weeks later, transparent crystals of various shapes from triangular to octagonal were observed on one of the flasks. They were collected and stored in a moisture free container. The following solubility tests were made on the crystals. The crystals were insoluble in ether, sodium

hydroxide, hydrochloric acid, acetone, and pyridine; but were very slightly soluble in cold water, and moderately soluble in hot water. Melting points for the crystals ranged from 76°C to 78°C. An Infra-red spectrum graph was obtained for the crystals. Since the crystals were present in very small amount, however further tests were neglected. No further crystals formation was noted for awhile. Again, unexpectedly, some crystals were seen growing in another one of the flasks (same shapes as the previous crystals). Solubility tests were the same as before. Melting point of the crystals was found to be from 76°C to 77°C. Another Infra-red spectrum graph was made.

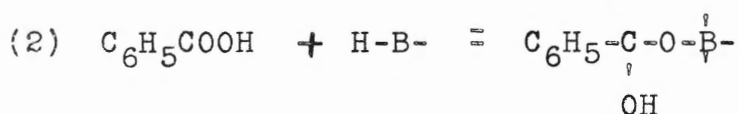
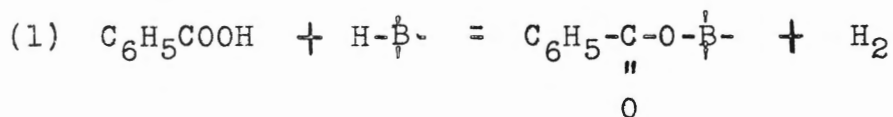
The following test for the presence of boron in the crystals was made: one milliliter of 1/24 N hydrochloric acid and one milliliter of 10% tumeric solution is added to a 10 cc sample in a porcelain evaporating dish, and the mixture evaporated to dryness slowly on a water bath. If boron is absent, the residue will not be pink; if boron is present, the pink or rose color may be used for estimation of the amount by comparison with a series of standards (22). In this test tumeric paper was substituted for the tumeric solution. The color of the tumeric paper was pale yellow before the test, and after the test the color turned pink. This test constituted a positive test for the presence of boron in the crystals. Melting point of the sodium tetraborate ($\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in the handbook of chemistry was found to be 75°C (10). Since the results were the same, it was concluded that the crystals formed were those of sodium tetraborate.

ISOLATION OF AN INTERMEDIATE FROM THE REACTION
OF SODIUM BOROHYDRIDE AND BENZOIC ACID

Considerations

Due to the fact that the reduction of benzoic acid by sodium borohydride failed to yield a large amount of the final product, it was speculated that some other kind of reaction was taking place during the course of the experiment. Although the identification of the intermediate was not of prime interest to this work, yet some preliminary tests were made in order to study them.

There are two methods by which sodium borohydride and benzoic acid might react. One of the methods involves the evolution of hydrogen gas. Equations for the two possible reactions are:



Compound (2) is essential for the formation of benzyl alcohol. The intermediate was insoluble in ether, soluble in hot water and in hot sodium hydroxide solution. It was quite soluble in pyridine, but slightly soluble in approximately 0.5 N HCl solution.

Experimental:

Run I - Sodium borohydride (1.0298 grams) and benzoic acid (6.5907 grams) were reacted. Gas evolution was noted at 125°C

and proceeded vigorously to 135°C . The reacted product was collected and then followed by two ether extractions, using 200 cc each of ether. The ether insoluble material was dried. Instead of refluxing with sodium hydroxide solution, cold distilled water (4°C) was substituted. Cold distilled water was used because hydrolysis of the material might occur at a higher temperature. Upon the addition of the cold distilled water to the dried ether insoluble product, foaming of the material occurred with part of it going into solution. The water insoluble material was dried and a melting point determination was made. The temperature kept increasing to 460°C with the following color changes noticed during the course of heating: white to gray to dark brown. Although such changes in color were noticed, yet the material did not melt. It finally decomposed.

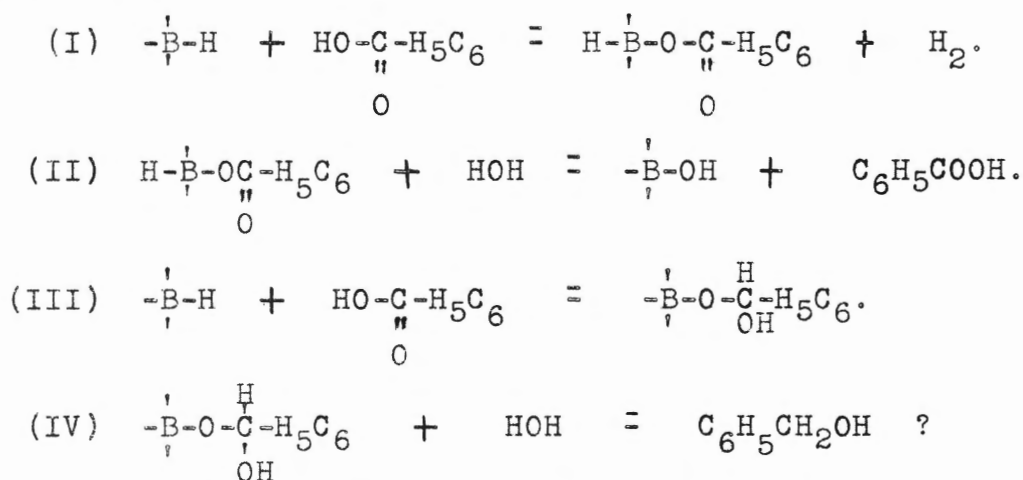
Run II - Sodium borohydride (2.4112 grams) and benzoic acid (30.8656 grams) were reacted. Gas evolution commenced at 129°C , became rapid as the temperature kept increasing to 140°C and then slowly subsided. The product was twice extracted with 200 cc volume of ether. The ether insoluble portion was dried, then washed with cold distilled water, and again dried. The material in the capillary tube melted around 140°C . Such a low melting point could only be accounted for by the presence of an excess of benzoic acid.

Run III - Sodium borohydride (2.3146 grams) and benzoic acid (14.8109 grams) were reacted. The ether insoluble material was dried and then washed with cold distilled water (2°C).

The solution was found to have a pH 8. The residue was collected and dried. At a temperature of 262°C part of the intermediate in the capillary tube melted. Another portion of the same material was rewashed and a melting point determination tried again. Temperature increased to 420°C., with the intermediate turning from white to gray. Again the material decomposed. The temperature could not be raised above 420°C because the apparatus was not capable of working at higher temperatures.

Run IV - Sodium borohydride (2.0000 grams) and benzoic acid (12.8021 grams) were reacted. The ether-insoluble product was washed with cold distilled water. The water-insoluble portion was collected and dried. During the melting point determination the temperature was increased to 434°C where charring occurred.

From the runs of this experiment, the mixture should consist of two compounds, one of which reacted with water more readily than the other.



The appearance of benzoic acid by treating the product of reaction (I) with water could be accounted for as due to the

ease of hydrolysis of the complex $\text{H}-\underset{\text{O}}{\overset{\text{O}}{\text{B}}}-\text{O}-\underset{\text{O}}{\overset{\text{O}}{\text{C}}}-\text{H}_5\text{C}_6$.

DISCUSSION

In the early part of this thesis the reduction of sodium borohydride with other organic compounds in the presence of a solvent was discussed. The work that was done here with sodium borohydride was based on the absence of a solvent. Results obtained from this research and the one which preceded it showed that solvents are not necessary for the formation of reductive products. In the case of acid chlorides, successful reduction was obtained by employing a suspension of sodium borohydride in dioxane or other inert solvent.

Direct mixing of the borohydride with acids especially if the acids were liquids in the presence of air was found extremely dangerous. Therefore, (1) liquid acids should always be cooled down to their freezing points. (2) Nitrogen gas should be bubbled through for at least fifteen minutes before the addition of the borohydride and fifteen minutes after the addition. (3) A safety screen should always be placed between the worker and the apparatus. (4) The sodium borohydride must be well dried and free from moisture. Failure to meet these requirements resulted in poor reaction if not an explosion.

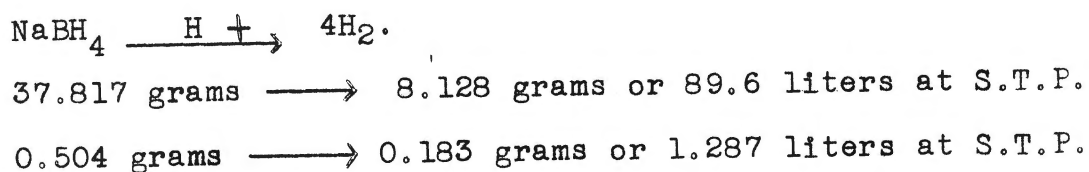
If during the course of the experiment air was let in, the white reactants immediately turned gray or black. The opening of the reaction flask during the experiment was done

only when (1) too much of reactants were used or (2) when the condenser was clogged with sublimed benzoic acid.

Reaction between sodium borohydride and benzoic acid were observed to initiate around 128° - 130° C, and to subside around 138° - 140° C.

From the reduction of benzoic acid by sodium borohydride, three products were identified. These were benzyl alcohol, sodium tetraborate and hydrogen gas. Although some examination was made with the intermediates no definite product was identified.

The reaction of one mole sodium borohydride at standard temperature and pressure should give 89.6 liters of hydrogen gas. From the results obtained in these experiments was established the fact that the reduction was not complete.

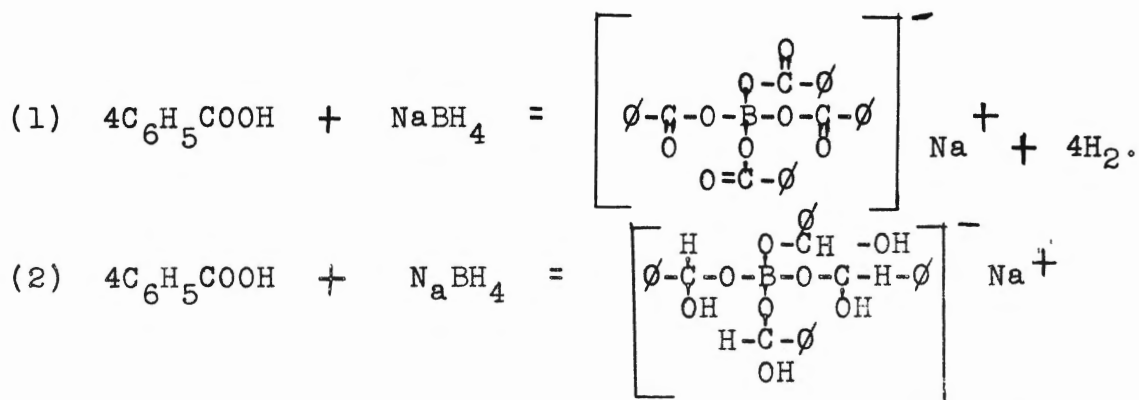


At a temperature of 26.1° C and at a pressure of 751.80 mm Hg.

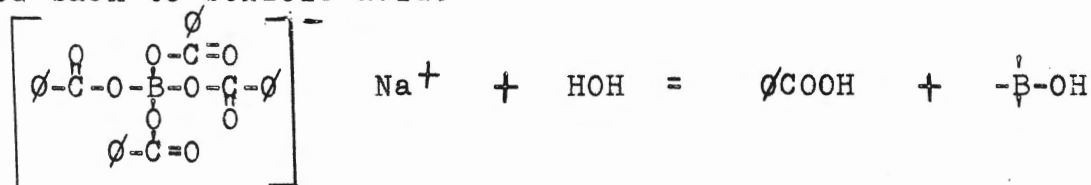


From experimental work 0.315 liter of hydrogen gas or 22.30% H_2 was obtained at 26.1° C and at a pressure of 751.80 mm. Hg. If the reaction were a complete one 1.412 liters of hydrogen gas would have been evolved. Therefore, the major portion of the reaction was the reduction of benzoic acid.

There appear to be two possible ways by which sodium borohydride and benzoic acid would react:



These two complexed would differ upon hydrolysis. The complex from reaction (1) would react more readily with water than the complex from reaction (2), because it would be easily hydrolyzed back to benzoic acid.



No free aldehyde, alcohol or acid were present in the ether insoluble portion of the reaction mixture. On hydrolysis both benzyl alcohol and benzoic acid were recovered. No aldehyde was obtained. From complex (2), two routes are possible. An additional molecule of benzoic acid could react to release benzaldehyde. The aldehyde would then react rapidly with more borohydride to form the reduced complex. The second alternative would be an attack by another borohydride on complex (2), thus reducing the aldol to the alcohol complex. In any event, the alcohol is produced only after hydrolysis.

The action of sodium borohydride on organic acids in the absence of a solvent follows the same pattern as reduction in the presence of solvents on all compounds except amides. It is now known that with amides the reduction products are formed directly.

The mechanism for the formation of sodium tetraborate- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ - from the remnant sodium hydroxide solution is unknown and leaves a field for further investigation.

The identification of the intermediates remains doubtful in spite of all of the efforts directed to this end.

SUMMARY

Sodium borohydride and benzoic acid were reacted in the absence of solvent. Three products were isolated and identified. These were (1) benzyl alcohol, (2) hydrogen and (3) sodium tetraborate. The alcohol was obtained only after hydrolysis of the reduction mixture.

Mechanism for the reaction of sodium borohydride and benzoic acid have been postulated for the formation of the two possible complexes. One of these complexes reacted readily with water giving back benzoic acid. This complex was easily hydrolyzed. The mechanism whereby the other complex gives benzyl alcohol upon hydrolysis has not yet been fully elucidated. Likewise, the mechanism for the formation of sodium tetraborate is still unknown.

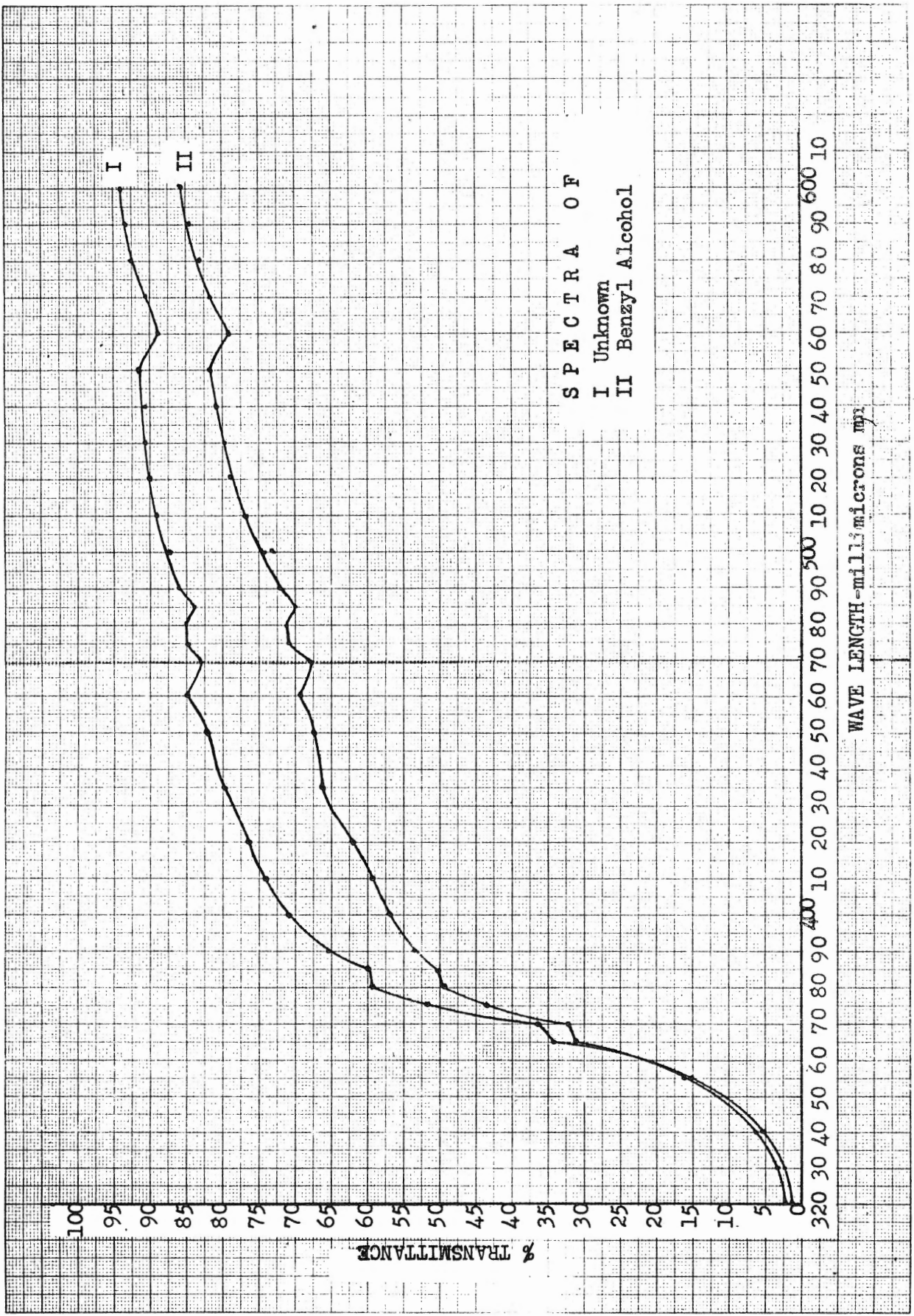
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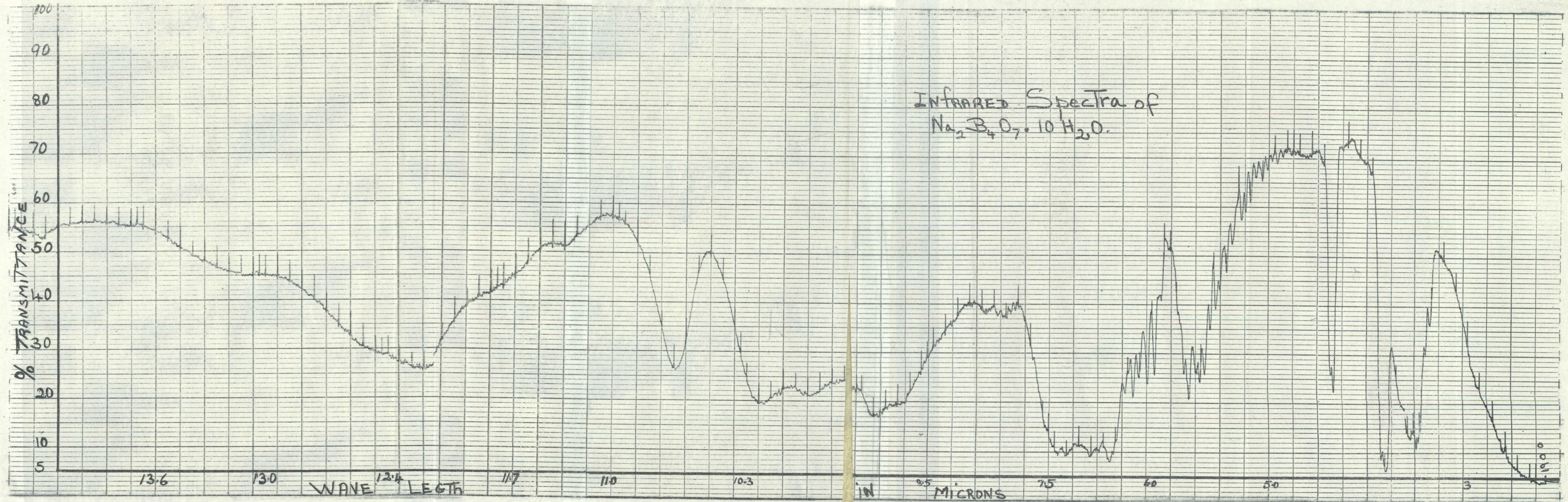
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APPENDIXES

- I. Spectra of Benzyl Alcohol and Unknown using Beckmann Spectrophotometer, Model DU.
- II. Infrared Spectra of Sodium Tetraborate.



SPECTRA OF
I Unknown
II Benzyl Alcohol



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Master of Science

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