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**CHEMICAL PROPERTIES OF SODIUM TRIETHYLHYDROBORATE
AND SODIUM TRIISOPROPOXYHYDROBORATE**

by

R. K. Pearson

L. J. Edwards

CALLERY CHEMICAL COMPANY
Callery, Pennsylvania

Technical Editor: P. M. Maginnity

Submitted by:

A. D. McElfoy

A. D. McElfoy
Supervisor, Research Department

Approved by:

G. F. Huff

G. F. Huff
Director of Research and Development

Callery Chemical Company
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ABSTRACT

Sodium hydride and triethylborane react to form sodium triethylhydroborate, $\text{NaBH}(\text{C}_2\text{H}_5)_3$. This compound, a liquid at room temperature, was found to be soluble in hexane and mineral oil. A study was made of the thermal decomposition of sodium triethylhydroborate and its behavior toward boron trifluoride, boron trichloride, methyl borate, carbon dioxide, silane, and ethylene.

Sodium triisopropoxyhydroborate, $\text{NaBH}(\text{OC}_3\text{H}_7)_3$, was prepared and also found to be soluble in hexane and mineral oil. The reactions of this compound with methyl borate, triethylborane, silicon tetrachloride, and boron trichloride were investigated.

CONTENTS

	Page
ABSTRACT	i
INTRODUCTION	1
RESULTS AND DISCUSSION	1
Sodium Triethylhydroborate	1
Sodium Triisopropoxyhydroborate	4
EXPERIMENTAL	5
Sodium Triethylhydroborate	5
Sodium Triisopropoxyhydroborate	8

INTRODUCTION

Brown, Schliesinger, Sheft, and Ritter⁽¹⁾ reported in 1953 that sodium hydride appeared to react with triethylborane in about a 1:1 ratio to give an oily, nonvolatile liquid. No analysis, however, nor any properties of this material were reported. If such a compound existed, it seemed desirable to verify its existence, as well as its composition, physical state, and characteristics, and to make a study of its reactions.

Sodium triisopropoxyhydroborate⁽²⁾ was first reported by Brown, Shoaf, and Tierney⁽²⁾. Except for its reducing ability toward organic compounds, this substance has not been investigated to any great extent.

The reaction of sodium hydride in a 1:1 ratio with triisopropoxyborane or triethylborane appears to be similar to the reaction of sodium hydride with methyl borate to give sodium trimethoxyhydroborate. Using suitable reagents and conditions, sodium trimethoxyhydroborate will yield sodium borohydride, dimethoxyborane, or diborane. Whether analogous reactions could be achieved in a simpler manner using sodium triisopropoxyhydroborate or sodium triethylhydroborate was the primary purpose of this investigation.

RESULTS AND DISCUSSION

The reactions of sodium triethylhydroborate and sodium triisopropoxyhydroborate described in the following sections were carried out largely in sealed tubes. The failure of any given experiment to produce the desired volatile boron hydride material may be in part due to the fact that the experiments were carried out in a static manner. The sealed tube type experiment was used in this study chiefly because it is more convenient experimentally and gives more reliable results than do flow systems.

Sodium Triethylhydroborate

Several sealed tube experiments were carried out to verify the observations of Brown, Schliesinger, Sheft, and Ritter⁽¹⁾ and to prepare sufficient quantities of sodium triethylhydroborate. Sodium hydride and triethylborane were found to react in ratios of very nearly 1:1. The product was a viscous, oily, nonvolatile liquid, soluble in hexane and in mineral oil. Sodium triethylhydroborate thus appeared to be a liquid compound. Such a liquid alkali metal compound, soluble in hydrocarbon solvents is quite unusual, and this compound should be considerably more reactive as a liquid than other solid, sodium borohydride type compounds. It was, indeed, found to be reactive toward water,

(2) Compounds of the type MBH_xR_{4-x} are named in this report in accordance with the rules proposed in "The Nomenclature of Boron Compounds", issued May 15, 1956 by the "Advisory Subcommittee on the Nomenclature of Organic Boron Compounds" of the American Chemical Society, and based on earlier recommendations of Schaeffer and Wartik (Chem. Eng. News, 32, 1441 (1954); *ibid.*, 34, 560 (1956)).

rapidly liberating hydrogen and triethylborane, and to be spontaneously inflammable in air. This is in contrast to the behavior of sodium trimethoxyhydroborate and sodium borohydride.

It was thought that thermal decomposition of sodium triethylhydroborate might yield alkyl diboranes, useful in themselves or capable of being converted to other products. This decomposition might occur in one of several ways. The compound could disproportionate to give sodium borohydride in a manner analogous to the disproportionation of sodium trimethoxyhydroborate. If such a reaction occurred, the ethyl analog of sodium tetramethoxyborate would be a highly interesting and perhaps useful material. Sodium triethylhydroborate might also decompose to liberate triethylborane or ethyl diboranes.

The results obtained from the pyrolysis of sodium triethylhydroborate at 145°C with pumping can best be interpreted in terms of a reversible decomposition to give triethylborane and sodium hydride:



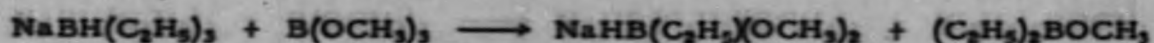
This path of decomposition appears to differ from the way in which sodium trimethoxyhydroborate decomposes (by formation of sodium borohydride and sodium tetramethoxyborate). The boron-hydrogen bond may be considerably weaker in sodium triethylhydroborate than in sodium trimethoxyhydroborate. The mode of thermal decomposition of sodium triethylhydroborate is reminiscent of the decomposition of lithium trimethylhydroborate⁽¹⁾.

The reaction of sodium triethylhydroborate with strong Lewis acids such as boron trifluoride or boron trichloride might be expected to produce boron hydride derivatives, since these acids can under proper conditions displace diborane from many variously substituted borohydrides. In a reaction between sodium triethylhydroborate and boron trifluoride in a sealed vessel at 70°C for 53 hours, about 15 percent of the hydride hydrogen was displaced to form volatile hydridic boranes. The low yield may be due to formation of the relatively stable compound sodium trifluorohydroborate, NaHBF_3 ⁽¹⁾, which is reported to result from the reaction of sodium trimethoxyhydroborate and boron trifluoride. If a similar reaction is carried out using ethyl ether-boron trifluoride, diborane is rapidly liberated. Therefore, it might also be expected that the yield of volatile boron hydrides could also be improved, using the ethyl ether-boron trifluoride with sodium triethylhydroborate.

When boron trichloride was used, however, essentially all the hydridic hydrogen of sodium triethylhydroborate was rapidly converted to volatile boron hydride compounds. Thus boron trichloride could effectively be converted to diborane via sodium triethylhydroborate and boron trichloride by the over-all reaction



An attempt was made to utilize methyl borate (a more readily available but weaker Lewis acid) to displace the hydride ion from sodium triethylhydroborate. It was thought that either dimethoxyborane or ethyl boron hydride derivatives might be obtained from this reaction. Instead, a large quantity of volatile diethylmethoxyborane was formed, together with a white solid which appears to have the empirical composition $\text{NaBH}(\text{OCH}_3)_2(\text{C}_2\text{H}_5)$. The principal reaction involved may be as follows:



These results suggest that methyl borate is too weak a Lewis acid to displace diborane (or diethylborane) from sodium triethylhydroborate.

Sodium triethylhydroborate was allowed to react with carbon dioxide in another attempt to displace ethyl boron hydrides. In this case, however, the carbon dioxide was reduced by the hydride, yielding sodium formate and triethylborane, but no diborane or other hydridic borane.



This behavior is completely analogous to the reaction of sodium trimethoxyhydroborate with carbon dioxide⁽¹⁾ in which sodium formate and methyl borate are formed.

To determine whether sodium tetraethylborate, the ethyl analog of sodium tetramethoxyborate, might be prepared, an attempt was made to initiate a reaction between sodium triethylhydroborate and ethylene. If a compound such as sodium tetraethylborate existed, it might help to confirm or to reject the postulated disproportionation of sodium triethylhydroborate to give sodium borohydride, similar to the disproportionation of sodium trimethoxyhydroborate. No reaction was observed, however, between ethylene and sodium triethylhydroborate after the reactants had been in contact for eight hours at 130°C.

Current investigations in this laboratory have shown that silane will react with sodium tetramethoxyborate to give sodium borohydride.



It seemed desirable to determine whether a similar reaction could take place with sodium triethylhydroborate. No reaction was observed, though, between silane and sodium triethylhydroborate after they had been in contact for 15 hours at 80°C. When the reaction was carried out at 250°C, much carbonization occurred, and a small quantity of material, possibly a mixture of ethyl silanes, was obtained. It is likely that the expected thermal decomposition of sodium triethylhydroborate occurred, followed by decomposition or reaction of the triethylborane.

Sodium Triisopropoxyhydroborate

Sodium triisopropoxyhydroborate was prepared by the methods of Brown, Shoaf, and Tierney⁽²⁾; i. e., by refluxing triisopropoxyborane with sodium hydride. The resulting compound was found to be soluble in mineral oil and hexane, and could readily be prepared from a mineral oil slurry of sodium hydride and triisopropoxyborane. This high solubility is quite unexpected, since sodium trimethoxyhydroborate (or other alkali or alkaline earth substituted borohydrides) is not soluble in these solvents. Because of its solubility, sodium triisopropoxyhydroborate ought to be much more reactive than other unsubstituted borohydrides, and much easier to prepare and handle than such compounds. It was primarily this unique behavior that prompted investigation of further chemical properties of sodium triisopropoxyhydroborate.

It was hoped that diborane, dimethoxyborane, or the isopropyl analog of dimethoxyborane could be readily prepared from sodium triisopropoxyhydroborate, using methyl borate as the Lewis acid. The formation of dimethoxyborane or diborane might be expected in this case, due to their lower volatility. No hydridic borane compounds resulted, however; when methyl borate was allowed to react with sodium triisopropoxyhydroborate. Instead, there was formed triisopropoxyborane, and also a solid with a composition equivalent to sodium trimethoxyhydroborate.



The composition of the solid was deduced from the nature of the volatile materials.

Since triethylborane is a compound of different acid strength from that of methyl borate, it seemed likely that alkyl boron hydrides, dimethoxyborane or the isopropyl analog of dimethoxyborane (diisopropoxyborane), might be formed by a reaction of triethylborane with sodium triisopropoxyhydroborate. Triethylborane appeared to react with sodium triisopropoxyhydroborate, however, to give a solid of the apparent composition $\text{NaBH}(\text{C}_2\text{H}_5)(\text{OC}_3\text{H}_7)_2$, and none of its hydridic hydrogen was displaced to form volatile hydrido boranes. The failure of triethylborane to produce volatile boron hydride compounds suggests that both triethylborane and methyl borate may be too weak as Lewis acids to displace ethyl diboranes, dimethoxyborane, or diisopropoxyborane.

Boron trichloride reacted with sodium triisopropoxyhydroborate in mineral oil at room temperature to give diborane and other boron hydride compounds. Approximately 72 percent of the hydridic hydrogen was displaced from the sodium compound to give volatile hydrido boranes. This yield is very good in view of the fact that mineral oil was used as a solvent and that the reaction was carried out at room temperature. It is highly probable that a larger yield could be obtained if excess boron trichloride were used, since some of the boron trichloride may have been converted to alkoxy derivatives of somewhat lower activity in the mineral oil medium.

Small quantities of both silane and diborane were obtained when silicon tetrachloride was allowed to react with sodium triisopropoxyhydroborate dissolved in tetrahydrofuran. Thus silicon tetrachloride is sufficiently acidic to effect the release of diborane, although it undergoes concurrent hydridic reduction.

EXPERIMENTAL

Sodium Triethylhydroborate

Preparation

Three experiments were made to verify the stoichiometry of the sodium hydride-triethylborane reaction. Sodium hydride (of a purity of 86 percent as determined by hydrogen evolved on hydrolysis) and triethylborane were added to 330 ml. evacuated flasks which were then sealed. The flasks were placed in an air oven at the desired temperature. Conditions used in each experiment and the molar quantities of reactants are shown in Table I.

TABLE I

Stoichiometry of the Reaction of Sodium Hydride and Triethylborane

Exp.	Time (hr.)	Temp. (°C)	NaH Used (mmoles)	(C ₂ H ₅) ₃ B Used (mmoles)	(C ₂ H ₅) ₃ B Recv'd. (mmoles)	Evolved H ₂ (mmoles)	React. Ratio NaH/(C ₂ H ₅) ₃ B	Unidentified Material (mmoles)
1	17.5	50	8.58	13.01	4.63(a)	0.227	0.996(b)	0.724(c)
2	32	70	8.79	13.93	5.91	0.301	0.946	0.775
3	44	65	10.33	15.52	4.87	0.306	0.942	0.861

(a) Vapor pressure, 14 mm. at 0°C.

(b) Correction of the quantity of NaH was made for the small quantity of hydrogen evolved (by subtracting the mmoles of H₂ from the mmoles of NaH charged) before the reaction ratio was calculated.

(c) Probably ethane or ethylene.

After the flasks had been opened to the vacuum system, hydrogen was isolated by means of a Toepler pump. Excess triethylborane was removed by pumping for several hours and separated from small quantities of more volatile material by passage through U-traps maintained at -78.5°C. From the quantities involved, it is evident that the sodium hydride and triethylborane reacted in a 1:1 ratio. This material was a dark, viscous liquid, but in subsequent preparation in which a purer sodium hydride was used, the product was a colorless viscous liquid.

Solubility in Mineral Oil and Hexane

The solubility of sodium triethylhydroborate in mineral oil and hexane was demonstrated by the following experiment:

A clear colorless solution resulted when a sodium hydride-mineral oil suspension and excess triethylborane were placed in a closed flask in the absence of air. After the excess triethylborane and some of the mineral oil had been removed by pumping in vacuum, a viscous yellow solution resulted. This yellow solution was soluble in hexane, and when water was added to the solution, hydrogen was rapidly evolved.

Thermal Decomposition

Sodium triethylhydroborate was prepared by allowing 11.98 mmoles of sodium hydride (of 87 percent purity) to remain for 20 hours at room temperature or slightly above in contact with 20.16 mmoles of triethylborane in a vacuum system. Volatile materials recovered were 0.41 mmole of hydrogen, 8.1 mmoles of triethylborane, and 1.16 mmoles of ethane. The dark nonvolatile liquid product of this reaction was then heated over a period of 1.5 hours to 145°C and maintained at this temperature while pumping for 3.5 hours. From this reaction, the volatile materials obtained were 4.28 mmoles of triethylborane, 0.90 mmole of ethane, and 1.58 mmoles of unidentified materials.

When the nonvolatile product resulting from the heating of the 11.57 mmoles of sodium triethylhydroborate was hydrolyzed, 9.82 mmoles of molecular hydrogen was obtained. Therefore, the product had decomposed largely to give triethylborane and presumably sodium hydride. The possibility that some alkyl diboranes were formed was not ruled out by this experiment.

Reaction with Boron Trifluoride

A mixture of 19.42 mmoles of boron trifluoride (vapor pressure 301 mm. at -111.9°C) and 8.49 mmoles of sodium triethylhydroborate (prepared as in Experiment 2, Table I) was maintained in a sealed flask for 53 hours at 70°-75°C. Upon opening the flask, the following volatile substances were obtained after fractionation and hydrolyses of certain fractions: Hydrogen, 0.72 mmole; a -112° to 196°C fraction, 17.47 mmoles; a -78.5° to -112°C fraction, 0.089 mmoles; and a room temperature to -78.5°C fraction (triethylborane), 0.773 mmole. Hydrolysis of the nonvolatile reaction products yielded 7.09 mmoles of hydrogen. Thus 15.5 percent of the hydride was displaced from sodium triethylhydroborate by boron trifluoride to give volatile hydride boranes.

Reaction with Boron Trichloride

A mixture of sodium triethylhydroborate (13.23 mmoles), prepared as described above, and boron trichloride (20.5 mmoles) was warmed in a sealed tube from -196°C to room temperature. A vigorous reaction took place with gas evolution and solid formation as the reaction vessel warmed. When the flask was

opened, 0.81 mmole of diborane was isolated by passage of the volatile reaction products through U-traps held at -131°C and -196°C (the diborane was retained in the -196°C trap). Hydrolysis of the -131°C fraction resulted in the formation of 8.33 mmoles of molecular hydrogen. Thus essentially all the hydridic hydrogen from sodium triethylhydroborate was converted to volatile hydrido boranes. The weight of white solid remaining in the flask (qualitatively identified as sodium chloride) was very close to the calculated amount of this compound.

Reaction with Methyl Borate

A mixture of methyl borate (20.86 mmoles) and approximately 10 mmoles of the above prepared sodium triethylhydroborate was maintained at 55°C for 17 hours in a sealed tube. During this time a white solid formed in the reaction vessel. Mass spectrometric analysis of the volatile materials obtained when the vessel was opened indicated the presence of methyl borate, ethyldimethoxyborane, diethylmethoxyborane, triethylborane, methane, ethane, and a small quantity of unidentified material.

From the quantities of these compounds, it was calculated that 10.0 mmoles of ethyl groups and 28.91 mmoles of methoxy groups were present in the non-volatile, white, solid reaction product, as well as 10.0 mmoles of sodium hydride and 13.8 milliatoms of boron. An X-ray powder pattern of this solid showed several unknown lines and other lines corresponding to those of sodium borohydride and/or sodium trimethoxyhydroborate. An infrared spectrum of the solid showed all bands of sodium trimethoxyhydroborate plus other unidentified bands. It is possible that the solid may contain a new compound, sodium ethyldimethoxyhydroborate, $\text{NaBH}(\text{C}_2\text{H}_5)(\text{OCH}_3)_2$.

Reaction with Carbon Dioxide

Sodium triethylhydroborate (8.35 mmoles), prepared as in Experiment 1 (Table I), and carbon dioxide (18.99 mmoles) were allowed to react in a sealed flask for 39 hours at 50° to 75°C . During this time a white solid formed. The volatile materials obtained from the reaction vessel were separated into four fractions: Hydrogen (0.04 mmole); carbon dioxide (15.56 mmoles); triethylborane (2.56 mmoles), and an unidentified fraction condensed between -78°C and room temperature (0.42 mmole). The nonvolatile solid remaining in the flask, when hydrolyzed with excess water, liberated 4.74 mmoles of hydrogen. Thus 3.61 mmoles of sodium triethylhydroborate was consumed along with 3.43 mmoles of carbon dioxide, and 2.56 mmoles of triethylborane was evolved. These data suggest that the following reaction occurred but was not completed:



In order to confirm the presence of the formate group in the nonvolatile reaction products, the nonvolatile products of hydrolysis of the solid reaction product were treated with concentrated sulfuric acid. Carbon monoxide (2.94 mmoles) was evolved, and identified by means of the mass spectrometer.

Reaction with Silane

Silane was quantitatively recovered after remaining in contact with sodium triethylhydroborate in a sealed tube for 15 hours at 80°C. In a second experiment carried out for three hours at 250°C, much carbonization occurred. Ethane, triethylborane, and part of the unreacted silane were recovered from the reactor in addition to a small quantity of material which was tentatively identified by its mass spectrum as a mixture of ethyl silanes.

Behavior with Ethylene

Sodium triethylhydroborate (12 mmoles) was allowed to react with 13.44 mmoles of ethylene in a sealed tube at 130°C for eight hours, but essentially all the ethylene was recovered, indicating that no detectable reaction had taken place.

Sodium Triisopropoxyhydroborate

Sodium triisopropoxyhydroborate was prepared by refluxing triisopropoxyborane (157.3 mmoles) with sodium hydride (90.61 mmoles) for three hours at atmospheric pressure. The reaction mixture was then pumped on a vacuum system at 70°C for two hours; the remaining white solid was crushed in a dry box and heated with pumping five hours in high vacuum at 100°C. The quantity of triisopropoxyborane recovered (65.2 mmoles) showed the reacting molecular ratio (triisopropoxyborane to sodium hydride) of very nearly 1:1 (1.017 to 1). Anal. (in mmoles/g.) Found, Na, 4.66; B, 4.90; hydrolyzable H, 4.18. Calcd. for $C_9H_{22}BNaO_3$, 4.72.

A 1:1 reacting ratio of sodium hydride to triisopropoxyborane was also observed when a sodium hydride slurry was refluxed with the alkoxy borane. A translucent solution resulted from which a yellow solid precipitated on further heating. The mixture turned to a paste on cooling, and this paste was quite soluble in hexane. Analysis of the hexane solution showed that sodium, boron, and hydridic hydrogen were present in a ratio of about 1:1:1. Assuming the soluble compound to be sodium triisopropoxyhydroborate, its solubility was of the order of 7 g. per 100 g. of hexane.

Reaction with Methyl Borate

A preliminary experiment showed that when methyl borate and sodium triisopropoxyhydroborate were allowed to remain in contact for three hours at 135°C, a reaction occurred in which triisopropoxyborane, isopropoxydimethoxyborane, and diisopropoxymethoxyborane were formed, identified by their mass spectra.

In a second experiment 1.801 g. of sodium triisopropoxyhydroborate (7.8 mmoles) and methyl borate (23.75 mmoles) were allowed to react at 90°C in a sealed tube for five hours. The quantities of volatile products recovered from the reaction vessel (0.60 g. more than the methyl borate charged) were

consistent with a reaction in which all the isopropoxy groups had been displaced by methoxy groups. These volatile products recovered from the reaction vessel were hydrolyzed with water, giving 23.88 mmoles of boron and 48.06 mmoles of methoxy groups (determined as methanol), but giving no evidence of hydridic hydrogen. Thus 23.19 mmoles of methoxy groups were consumed in the reaction, compared to 7.8 mmoles of sodium triisopropoxyhydroborate used (a ratio of very nearly 3:1). The following reaction would satisfactorily explain these results:



Since excess methyl borate was used, there were mixed alkoxy boranes present in the volatile reaction products rather than pure triisopropoxyborane.

Reaction with Triethylborane

Refluxing a mixture of sodium triisopropoxyhydroborate and triethylborane for 22 hours caused the nonvolatile solid to lose weight approximately equal to that expected if the sodium triisopropoxyhydroborate had been converted to $\text{NaBH}(\text{C}_2\text{H}_5)(\text{OC}_3\text{H}_7)_2$. The X-ray powder pattern of the solid reaction product did not correspond to that of the starting sodium triisopropoxyhydroborate.

Reaction with Silicon Tetrachloride

Silicon Tetrachloride (2.51 mmoles) and sodium triisopropoxyhydroborate (9.8 mmoles) were allowed to remain in contact at room temperature for 16 hours in the presence of 5 ml. of tetrahydrofuran. Approximately 40 percent of the hydridic hydrogen charged as sodium triisopropoxyhydroborate was converted to diborane and silane (identified by their mass and infrared spectra) of which about 75 percent was diborane.

Reaction with Boron Trichloride

Sodium triisopropoxyhydroborate (7.94 mmoles), boron trichloride (3.78 mmoles), and 10 ml. of mineral oil were placed in a sealed tube at -196°C . As the tube was allowed to warm to room temperature, vigorous bubbling occurred initially with evolution of heat. After 15 hours the flask was opened and was found to contain 0.43 mmole of hydrogen and 0.494 mmole of diborane. Hydrolysis of the remaining volatile reaction products gave 5.36 mmoles of hydrogen. Thus at least 72 percent of the hydridic hydrogen of the substituted borohydride was converted to hydridic hydrogen of volatile boranes.

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Experimental Notebooks:

R. K. Pearson	CCC-1184
N. J. Sheetz	CCC-1231
T. W. Platt	CCC-1303

END