

SODIUM BOROHYDRIDE AND AMINE-BORANES, COMMERCIALY
IMPORTANT REDUCING AGENTS

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Abstract - Sodiumborohydride, NaBH_4 (I) and amine-boranes, $\text{R}_2\text{NH}-\text{BH}_3$ (II) are widely used reducing agents in organic and inorganic chemistry. A survey of the application of I and II in the selective reduction of various organic groups is given. The field of metallisation by chemical means, using I and II, especially the chemical nickel-plating of metallic and nonmetallic substrates attracts more and more scientific as well as industrial interest. These and other applications of I and II together with synthetic routes leading to these reducing agents are discussed.

INTRODUCTION

Although sodium borohydride and its derivatives range far behind the other commercially used boron compounds such as borates or boric esters - it is estimated that in terms of quantity less than 1 % of all boron compounds sold accounts for this group of products¹⁾ - in recent years they have gained a remarkable position of increasing importance on the market for high quality special chemicals.

Today sodium hydride is produced in the Western World in the order of 1000 tons/year. At prices of approx. DM 70.00 per kg (for solid 98 % NaBH_4) this is a multimillion dollar business. A paper on sodium borohydride and amine-boranes with emphasis on the technical side of these materials would thus appear to be quite in line with the scientific character of this meeting.

In 1976 the demand for NaBH_4 will undergo a substantial increase with the commissioning of a new commercial scale plant set up at a capital expenditure of 12 million dollars in Elma, Washington, USA, to supply the Canadian and US paper industry in the Northwest of the American Continent²⁾. Plans have also been made to produce sodium borohydride in Japan³⁾. The most important commercial derivatives of NaBH_4 , the amine-boranes are produced on a considerable smaller scale, although tonnage quantities are already involved⁴⁾. That sodium borohydride has developed over the last few years into an interesting product in terms of quantity must be attributed to the opening-up of new applications beyond organic synthesis, e.g. in the bleaching of wood pulp, the purification and stabilization of organic materials and the chemical separation of metals. In addition, intensive research work revealed further applications in preparative chemistry. In these applications the reducing effect is accurately controlled by modifying the reaction conditions such as temperature, pH, solvents, presence of catalysts or activating groups in the molecule to be reduced and consequently the use of NaBH_4 has considerably widened beyond the classical application of converting aldehydes and ketones into the corresponding alcohols. Finally, sodium borohydride is a complex hydride, allowing satisfactory handling in air, and can often be used in water as solvent. There is even an alkaline solution of NaBH_4 commercially available. In spite of the relatively high price, at least for the solid, pure product, its high content of 10.6 % active hydrogen (1 reduction equivalent weighs 4.73 g) gives costs per unit of hydrogen which are attractive in many cases.

In a recent cost comparison NaBH_4 compares favourably with other hydrides used as reducing agents such as lithium aluminium hydride or sodium-(2-methoxyethoxy) aluminium hydride⁵⁾.

TABLE 1

	Price (\$ per pound)	Molecular weight	Weight % of active hydrogen	Cost of active hydrogen (\$ per pound)	Amount of hydride purchased (pounds) ^{a)}
NaBH ₄	13	37,8	10,6%	123	1 000
LiBH ₄	50	21,7	18,3	273	1 000
KBH ₄	18	53,9	7,4	243	100
LiAlH ₄	28	37,9	10,6	265	1 000
NaBH ₄	24	54,0	7,4	324	1 000
NaBH ₃ CN	15	62,8	4,8	313	1 000
(iso-C ₄ H ₉) ₂ AlH	1,50	142,2	0,7	213	1 400
NaAl(OC ₂ H ₄ OC ₂ H ₃) ₂ H ₂	3,58	208,1	1,0	360	14 600
NaAl(C ₂ H ₅) ₂ H ₂	2,75	110,1	1,8	151	400
LiAl(O-tert-C ₄ H ₉) ₃ H	25	257,2	0,4	6 410	1 000
Al(C ₂ H ₅) ₂ H	1,40	86,0	1,2	117	1 000

a) Amount of hydride purchased for prices shown in table

Sodium borohydride was discovered by H.J.Schlesinger et al. of Chicago University as early as 1942 while looking for volatile uranium compounds, e.g. U(BH₄)₄. Because of war-time secrecy the synthesis could not be published prior to 1953⁶⁾. The fascinating story of the discovery of this and affiliated compounds and the discovery of the first applications, e.g. solvolysis in the presence of cobalt salts for the production of H₂ or the reduction of acetone to isopropanol has recently been retold in a humorous way by H.C.Brown, the well-known pioneer in the borane field⁷⁾.

However, Alfred Stock had already come across contaminated NaBH₄ since the so-called hypoborates obtained in the reaction of boranes (B₂H₆, B₄H₁₀) with strong alkaline solutions contain alkali borohydrides⁸⁾⁹⁾. He also found that potassium hypoborate, KOBH₃, reacts with aqueous nickel-salt solutions at room temperature to form nickel boride, Ni₂B, a reaction which Stock considered notable since borides are otherwise only accessible through high temperature reactions. In a manner of speaking this is the first indication of electrodeless nickel plating, today an important application of sodium borohydride¹⁰⁾. Also in the reaction of alkali amalgams with diborane. Stock obtained products with, the composition Na₃B₂H₆ which, as recent investigations have shown, contain alkali borohydrides⁶⁾¹¹⁾.

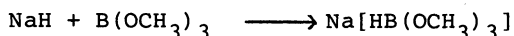
The commercial importance of sodium borohydride and its derivatives reached its first peak in the fifties when under several U.S. military programmes there was intensive work on the development of boron-based high energy fuels for rockets and high altitude jets¹²⁾. The boron fuels (alkylpenta- and -decaboranes) which were already produced by several firms in the order of tons met with wide interest since their heat of combustion is up to 50 % higher than that of conventional hydrocarbon fuels. In those years substantial capacities were set up for production of boranes and their starting products, such as sodium borohydride, which, following the well-known negative outcome of the programme, could be little utilized since non-military applications were limited. The large plant of Ventron Co., the former Metal Hydrides Inc., for the production of NaBH₄, in Danvers, Mass., dates from this time. The plant was set up in 1958, mainly financed with government funds. But as early as 1959 the U.S. Navy contract for supplies of NaBH₄ was cancelled and this gave rise to acute economical problems¹³⁾. These could only be overcome as new applications were found for NaBH₄ in the paper and textile industries. Sodium borohydride is marketed today in three commercial forms: as a pure 98 % powder, in the form of pellets, and as an aqueous solution containing 12 % NaBH₄ and 40 % NaOH. Commercially available derivatives are quaternary ammonium borohydrides, sodium cyanoborohydride, lithium and potassium borohydride, the sulphur derivative NaBH₂S₃ and diborane (e.g. in gas mixtures with N₂, Ar or H₂; as solution in tetrahydrofuran and as an adduct with dimethyl sulphide) and amine-boranes (e.g. dimethyl and diethylamine-boranes, pyridine and morpholine boranes, t-butylamine-borane)¹⁴⁾. In Germany Bayer AG worked on the synthesis of NaBH₄ starting in the mid-fifties and since 1957 a commercial plant has been in operation. Since the mid-sixties we are also producing amine-boranes with emphasis on the dialkylamine-boranes.

PRODUCTION OF SODIUM BOROHYDRIDE AND AMINE-BORANES

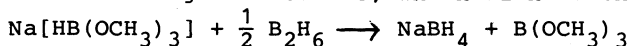
A large number of suggestions and approaches to the synthesis and isolation of metal borohydrides, especially NaBH₄, is found in the literature and reflected in nearly 100 patent publications. A synopsis is given by F. Schubert and K. Lang¹⁵⁾. However, only two processes have gained commercial importance: the boric acid ester process developed in the USA, and the borosilicate process from our laboratories. The fluoroborate process investigated in the USSR has only been developed to pilot plant scale.

The boric acid ester process

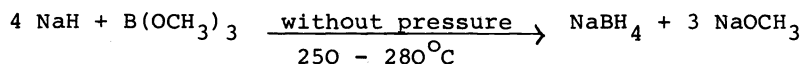
The process originates from studies by H.H. Schlesinger et al. who found that at a relatively low temperature, sodium hydride reacts with trimethyl borate as follows



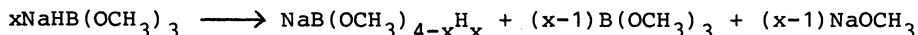
to give sodium trimethoxy borohydride. This reacts with borontrifluoride etherate to give diborane, which with further borohydride forms NaBH₄



Experiments aimed at the production of sodium borohydride without using diborane finally led to the synthesis from sodium hydride produced in situ finely dispersed in a high boiling mineral oil, and trimethyl borate at approx. 250 - 280°C:



Important features of this synthesis are the necessity of operating under accurately defined stirring conditions and the importance of the grain size of the hydride. The reaction temperature should be relatively high (250°C) for the reaction to proceed rapidly through the interim formation of NaHB(OCH₃)₃ (with a melting point of 230°C) thus avoiding the liquid phase; the reaction runs as follows:



Disproportionation is complete at 280°C¹⁶⁾. Excess of boric acid ester should be avoided because sodium tetramethoxyborate is formed which contaminates the borohydride.

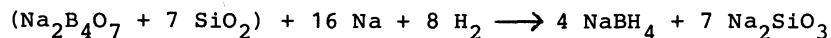
In commercial operation, NaBH₄/NaOCH₃ separation is effected by dissolving the reaction mixture in water, separation of the methanol thus formed followed by liquid/liquid extraction of the NaOH-containing aqueous solution with isopropylamine¹⁷⁾. The NaBH₄-containing, aqueous, amine solution is evaporated and the borohydride is isolated as the dihydrate. Careful heating in vacuum gives pure NaBH₄.

Synthesis of potassium borohydride has also been effected on a commercial scale by reacting the alkaline aqueous methanol NaBH₄ solution with KOH which causes the difficultly-soluble KBH₄ to be precipitated¹⁸⁾. The required ester is produced from boric acid and methanol and the resultant azeotropic mixture of B(OCH₃)₃ and CH₃OH (73/27 % by wt.) is separated with a methanolic lithium chloride solution¹⁹⁾. While the boric acid ester process is a multi-stage process, it offers the advantage of operation at a relatively low temperature in the liquid phase. A disadvantage is the expense of boric acid as a starting material. A useful feature, on the other hand, is that a marketable sodium alkaline NaBH₄ solution - which is much cheaper than solid NaBH₄ - is directly obtained in the course of the process.

The borosilicate process

The process used by Bayer starts with cheaper boron sources such as borax or Ulexite (calcium sodium borate) and is completed in three stages¹⁵⁾. However, synthesis takes place at higher temperatures, 400-500°C, under a H₂ pressure of some bars in a partially-solid reaction.

At first, e.g. a borosilicate glass is fused from borax and quartz sand and this is allowed to react with metallic sodium and hydrogen in a reaction scheme as per



The borohydride/silicate mixture obtained is extracted with liquid ammonia under pressure; pure crystalline NaBH₄ is left after the NH₃ has been evaporated.

Instead of SiO_2 as the sodium oxide binding agent it is possible to use aluminium in the reaction between sodium hydride and dehydrated borax; as per:

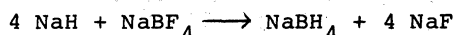
$$2 \text{Na}_2\text{B}_4\text{O}_7 + 7 \text{Al} + 11 \text{Na} + 16 \text{H}_2 \longrightarrow 8 \text{NaBH}_4 + 7 \text{NaAlO}_2$$
 less sodium is necessary²⁰⁾.

The resultant mixture is hydrolyzed and the borohydride extracted with isopropylamine. A disadvantage is the necessity of conducting the reaction at higher temperatures, e.g. 500°C , than are used in the borosilicate process. This reaction, however, already gives appreciable quantities of sodium dodecahydrido-dodecaborate $\text{Na}_2\text{B}_{12}\text{H}_{12}$ which is known to be the most stable hydrido-borate thermodynamically²¹⁾.

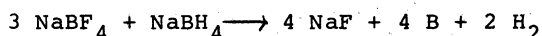
From this observation we succeeded in developing a selective synthesis of this interesting icosahedral higher borohydride, the chemistry of which had been closely investigated by Muetterties et al.²²⁾ at DuPont.

The Fluoroborate process

A few years ago the Czechoslovak Academy of Sciences studied the reaction of very finely dispersed sodium hydride with sodium tetrafluoroborate at $260 - 280^\circ\text{C}$ in an oil suspension²³⁾, as per:



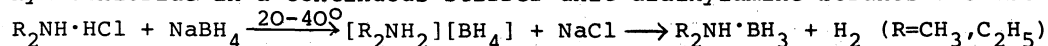
The borohydride is isolated by NH_3 extraction. Being a straight forward solid reaction the process is carried out continuously in a thin film reactor at 5 - 10 bar H_2 pressure and the mixture obtained on completion of the reaction is immediately removed to suppress the objectionable side reaction



The process has not been further developed, presumably for marketing reasons. A certain disadvantage is likely to have been that sodium fluoride, presumably contaminated, was inevitably obtained.

Production of dialkylamine-boranes

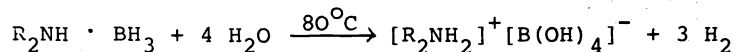
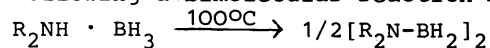
When reacting sodium borohydride in aqueous toluene solution with an amine hydrochloride in a continuous stirrer unit dialkylamine-boranes are obtained²⁵⁾



We have also investigated the reaction of the dimethylamine- BF_3 -adduct with sodium borohydride in tetrahydrofuran or dioxan.

This leads to the formation of the BH_3 -adduct of dimethylamine²⁶⁾. However the reaction is incomplete and the amine-borane is therefore contaminated with the BF_3 -adduct.

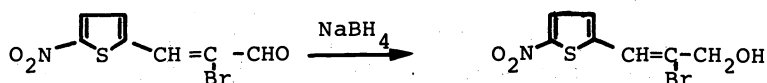
Let me briefly discuss the pyrolysis of the dimethylamine-borane. At an elevated temperature dimethylamine-borane eliminates hydrogen, presumably following a bimolecular reaction mechanism²⁷⁾.



However, when giving this heat treatment in the presence of water, hydrolysis takes place. A miscibility gap exists in the system dimethylamine/water²⁸⁾.

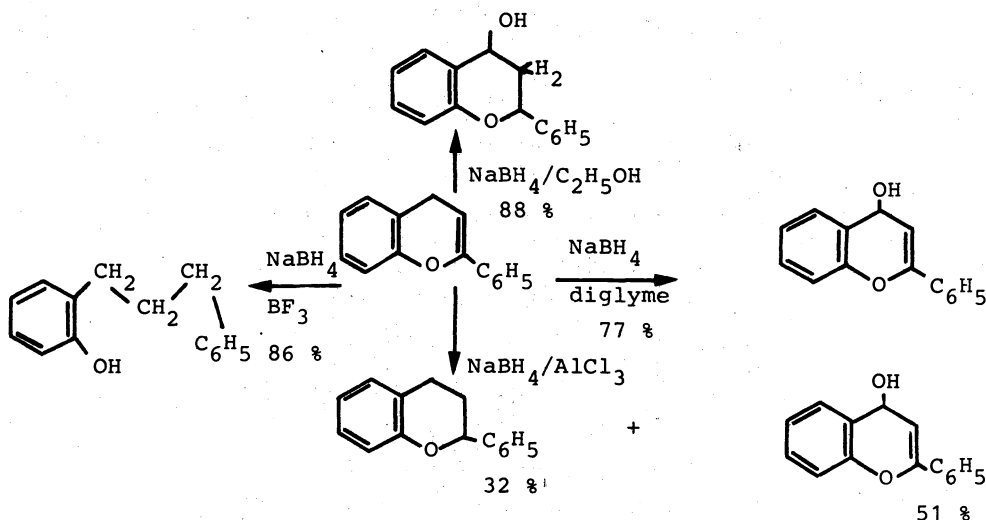
SODIUM BOROHYDRIDE AND AMINE BORANES AS SELECTIVE REDUCING AGENTS IN ORGANIC SYNTHESIS

Sodium borohydride is widely used in organic synthesis as a mild reducing agent of selective and also stereospecific action^{29), 30), 31)}. It is normally suitable for use without excluding atmospheric oxygen or moisture. An additional advantage, in contrast to lithium aluminium hydride, is that it has sufficient resistance to a number of solvents - in which it is dissolved or suspended - to allow corresponding reductions to be carried out in these solvents. Primarily water and alcohols, but also amines and ethers such as tetrahydrofuran, dioxan, diglyme or triglyme can be used as reaction media. The selective reduction effect is impressively shown by the classical example of the reduction of α -bromo- β -(5-nitro-2-thienyl)-acrolein³²⁾:

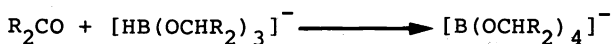
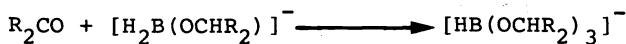
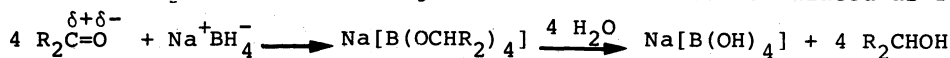


The aldehyde group is hydrogenated without any attack on the nitro group, the bromine atom or the olefinic double bond or the thiophene ring.

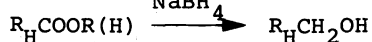
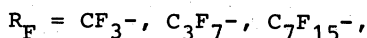
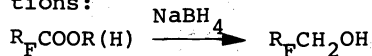
Another more recent example shows that NaBH₄ has a widely differing reactivity as a function of the reaction conditions³³⁾:



The reaction mechanism in the reductions with complex hydrides has not yet been elucidated in detail. To start with, a bimolecular nucleophilic addition is considered as certain. The hydride anion adds to the positively charged carbon atom and the positive radical of the complex hydride adds to the electronegative oxygen atom. The tetraalkoxy complex is then decomposed with water to give the corresponding alcohol³⁴⁾: This proceeds through four successive steps which according to H.C. Brown can be formulated as follows:



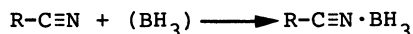
The observed kinetics show in the first step a slow reaction governing the rate, whereas the ensuing steps proceed considerably more quickly. From this mechanism it follows that groups inductively reinforcing the positive charge of the carbon atom favour the reaction whereas groups with the opposite effect inhibit it. For example, we found that perfluorinated carboxylic acids or esters are reduced with NaBH₄ to the 1,1-dihydroperfluoroalkanols³⁵⁾, whereas the non-fluorinated compounds were not reduced under identical conditions:



Besides aldehydes and ketones, sodium borohydride also reduces acid chlorides, peroxides, Schiff basis, quaternary halides and certain other functional groups. The reduction effect can be modified by the nature of the solvent, by changing the temperature and the NaBH₄ level. It can be increased in particular by using metal halides such as LiCl, CaCl₂, AlCl₃ etc. A particularly strong, yet selective reduction system (and also hydroboration agent) is a solution of anhydrous aluminium chloride with NaBH₄ in diglyme.

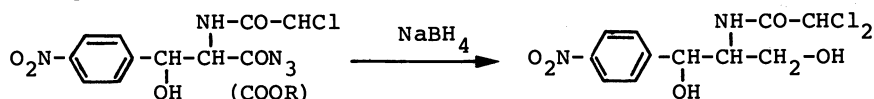
Similar to lithium aluminium hydride it will reduce carboxylic acids, esters, anhydrides and nitriles.

The nature of this hydroboration agent, a clear solution of 3 moles NaBH_4 and 1 mole AlCl_3 in diglyme, has recently been elucidated by H. Nöth³⁶⁾. The active species is the B_2H_7^- ion formed by a complex mechanism. The range of reactions is further widened by the possibility of producing diborane easily in situ from NaBH_4 and BF_3 in ethers. Being an electrophilic reagent and a strong Lewis acid, diborane has other reducing properties than the nucleophilic salt-like sodium borohydride. For example, nitriles are rapidly reduced by diborane through the electrophilic action on the nitrogen of the CN group, whereas NaBH_4 does not react.

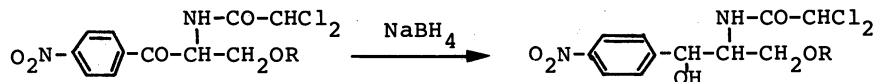


The reaction then proceeds forming the corresponding N,N,N" trialkyl borazines which are then hydrolyzed to give the amines. Esters, carboxylic acids and epoxides are also reduced.

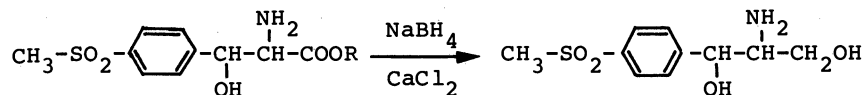
In the pharmaceutical industry sodium borohydride is used, for example, in the production of the chloramphenicol and thioamphenicol antibiotics. This has been widely recorded in literature; two approaches to synthesis using NaBH_4 in the last step are shown:



The acid azide or ester group is selectively reduced to the primary alcohol without attacking the nitro or acid amide group. In another synthesis the NaBH_4 reduction is carried out in an earlier step³⁸⁾.



In the synthesis of the similarly interesting thioamphenicol, the ester group is reduced³⁹⁾:

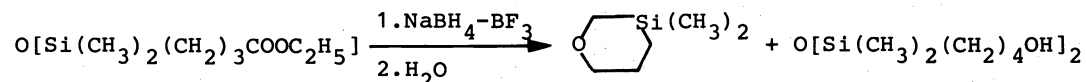
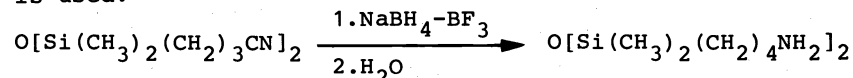


A particularly important factor in steroid chemistry is the stereospecific and selective reduction of steroid ketones offering the possibility of utilizing the differing reactivities of the ketone groups⁴⁰⁾. While recent publications show that sodium borohydride can enter further reactions it would be beyond the scope of this paper to deal with them.

SODIUM BOROHYDRIDE IN SILICONE CHEMISTRY

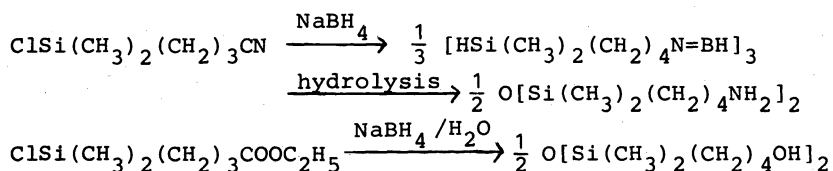
In this field we have been closely engaged, investigating organofunctional silicon compounds containing amines and alcohols starting from nitriles and esters⁴¹⁾.

The advantage of NaBH_4 -containing reduction systems over for example, lithium aluminium hydride, is that siloxane bonds are not cleaved. In the case of Si-Cl-free silicon compounds a mixture of NaBH_4 + BF_3 in tetrahydrofuran is used:



In the second case either 2,2-dimethyl-1-oxa-2-sila-cyclohexane is formed as a cyclic anhydride or the diol 1,3-bis-(4-hydroxybutyl)-tetramethyldisiloxane is formed, depending on the processing conditions.

A remarkable feature is the possibility of omitting the BF_3 addition in the presence of Si-Cl bonds in the unreduced molecule. The NaH component in the sodium borohydride converts the Si-halogen bond into an Si-H-bond in this case and the released borane then attacks the nitrile or acyl group electrophilically, e.g.:



To avoid the formation of BH₃, which is isolated as an amine-borane in the presence of triethylamine, it is also possible to solvate a part of the chlorosilane with methanol and to reduce then the molar mixture of the two silanes.

HYDROBORATION

Brief reference only is made in this paper to the well known hydroboration reaction, which is strictly the Anti-Markownikoff-addition of BH bonds to C-C-double or triple bonds, since comprehensive monographs and excellent synoptic publications are available^{(42), (43), (44), (45)}. This reaction was discovered in 1956 by H.C. Brown et al.^{(7), (46)} when reducing ethyl oleate with NaBH₄/AlCl₃ in diglyme during which surprisingly the hydroboration of the C-C-double bond occurred in addition to the reduction of the ester group. Since this time the hydroboration has been developed to become a highly valuable preparative method since the resultant organoboranes are accessible to a wide variety of reactions. The most important consecutive reaction is their oxidation to alcohols which correspond to a cis-hydration of the C-C-double bond. Besides diborane produced from NaBH₄ in situ, borane/tetrahydrofuran and borane/methyl sulphide complexes are also commercially available. Partially alkylated, sterically-hindered boranes are also used which are hydroboration reagents of improved selectivity and stereospecificity, e.g. for the synthesis of prostaglandins⁽⁴⁷⁾. In particular 9-BBN (9-borabicyclo(3,3,1)-nonane), which is stable in air, allows a simple procedure⁽⁴⁸⁾. In addition to the use of alkyl boranes for synthesizing natural materials, pharmaceuticals and fine chemicals, they also appear to be suitable for use in industrial petrochemistry⁽⁴⁹⁾.

The section on sodium borohydride is completed with the reference to its commercial use in the purification and stabilization of organic products such as alcohols, epoxides, amines, ethers and hydrocarbons. This removes objectionable impurities such as aldehydes, ketones and peroxides, even traces of which cause discoloration.

AMINE-BORANES IN ORGANIC CHEMISTRY

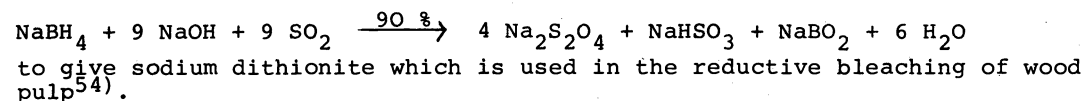
Similarly to sodium borohydride, amine-boranes are also suitable for use as selective reducing agents in organic chemistry. They offer some advantages over sodium borohydride such as good solubility in organic solvents and they are less sensitive to acids. This makes it possible, for example, to carry out reductions in acetic acid solution⁽⁵⁰⁾. On the other hand, they are normally weaker reducing agents.

In terms of reducing action they range between the electrophilic diborane and the nucleophilic complex borohydrides. Amine-boranes, for example, convert aldehydes, ketones and acid chlorides into the corresponding alcohols; they also reduce quinones, azomethines and, in special cases, carboxylic acids⁽⁵¹⁾. The rate of reaction increases with the acidity of the solution when reducing aldehydes⁽⁵²⁾. In solvents such as liquid SO₂ and nitromethane, trimethyl amine-borane reduces aralkyl halides to the corresponding hydrocarbons⁽⁵³⁾. At elevated temperatures amine-boranes are also suitable for use in hydroboration reactions.

A technically interesting aspect is the use of tert.-butylamine-borane as a nucleation agent in the developing of colour films⁽⁴⁾.

NaBH₄ AND AMINE-BORANES IN INORGANIC CHEMISTRY

These materials are also widely used. One of their applications is the reaction of sodium borohydride with sulphur dioxide as per



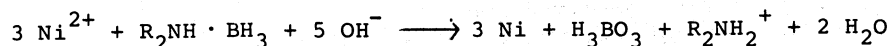
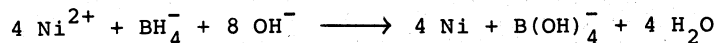
NaBH_4 is also used in the separation of metals from very dilute solutions such as mercury, cadmium, copper, gold, silver and platinum metals⁵⁵). The mercury removal from chlorine/alkali electrolysis effluent is expected to be effective down to the ppb range. It is also possible to remove mercury from mercury contaminated fish protein concentrates⁵⁶).

A discussion of the uses of NaBH_4 and amine-boranes in inorganic chemistry must necessarily include chemical nickel plating, also called electrodeless nickel plating. This process comprises the deposition of the nickel plate by means of reducing agents rather than by electric current.

Sodium borohydride-containing nickel plating baths have been developed in the second half of the fifties and adopted in commercial practice in the mid-sixties⁵⁸). These chemical nickel platings offer a number of advantage over electrolytic nickel plating.

These include the deposition of the nickel plate in uniform thickness on intricate articles which it would be difficult, if not altogether impossible to plate electrolytically. Following suitable surface treatment it is also possible to plate chemically semi-conducting or non-conducting substrates such as ABS plastics. Further metal plates can be electrolytically applied without any problem to the chemically applied conductive nickel coat. Another advantage of chemical nickel plating is that the resultant plate consists of boron- or phosphorus-containing nickel alloys which feature particularly favourable chemical, physical and mechanical-technical data. Particularly outstanding are the hardness and wear properties, the soldering performance and the corrosion resistance of these plates.

Nickel ions are reduced in the chemical nickel plating by sodium borohydride or amine-boranes in line with the following theoretical equations



The redox potentials of the corresponding redox pairs taking part in the metallization reaction are to ensure that these redox reactions proceed spontaneously and voluntarily with metal deposition. It would therefore appear to be difficult to prepare a nickel salt and reducing agent containing bath of adequate stability. Fortunately enough, however, reaction inhibitions are rather frequent, or inversely the baths for reductive metallization are thermodynamically unstable while having sufficient stability kinetically. This reaction inhibition can be overcome by supplying heat - most metal plating baths are run at elevated temperature - or by catalysts. Such catalysts are many of the metals known as hydrogenation catalysts such as palladium, silver, nickel, iron or platinum. The nickel deposition takes place with preference where such catalyst nuclei are present.

Once nickel has been deposited there the reaction continues since the nickel surface as such has a catalytic effect. From this follows that chemical nickel plating is a heterogeneous, quasi-autocatalytic redox reaction which, however, is always accompanied by a decomposition of the reducing agent with elimination of hydrogen so that the industrially-interesting reduction yield is in most cases below 50 %.

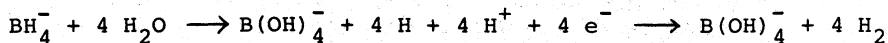
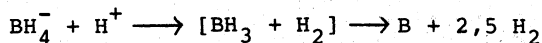
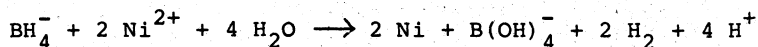
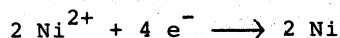
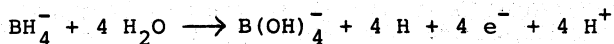
To destroy extraneous catalyst nuclei carried along into the solution, stabilizers, or more aptly inhibitors, are added to the metallizing bath. These are metal salts of e.g. cadmium or zinc or they are organic sulphur compounds of the +2 oxidation state. To avoid the formation of insoluble nickel hydroxide, sequestering agents are also added to reduce the nickel ion concentration. Such sequestering agents are dicarboxylic acids or amines such as ethylene diamine.

A typical bath formulation is as follows:

30	g/l $\text{NiCl}_2 \times 6 \text{H}_2\text{O}$
50 - 60	g/l ethylene diamine
40 - 50	g/l NaOH
20 - 30	mg/l stabilizer
0,2 - 0,3	g/l NaBH_4

The deposition rate of the nickel ions is 15 - 20 $\mu\text{m}/\text{hour}$ and depends on the concentration of metal ions, the reducing agent, the temperature and the pH.

The mechanism of these reactions has not yet been fully established. From mass spectroscopic measurements of the isotope composition of gaseous hydrogen which is formed during nickel plating with sodium borohydride in heavy water GORBUNOVA⁵⁹) draws conclusions to the following part reactions:



It follows that the H-atoms formed during hydrolysis do not take part in the Ni²⁺ reduction but combine to form H₂ molecules.

In chemical nickel plating with amine-boranes it is assumed that the first step is the adsorption and subsequent dissociation of the amine-borane molecule to a catalyst particle on the surface of the matrix resulting, among other effects, in the formations of boron⁶⁰). The Pd .. BH₃ complex formed as a catalyst in the case of palladium can either be decomposed to form boron and hydrogen or hydrolyzed to give boric acid and hydrogen and in this respect the relation of the two reaction rates, and consequently the boron content in the deposit, are influenced by various parameters such as temperature and pH. The resultant hydrogen is chemically adsorbed to the catalyst surface either in molecular form or as hydride ion and this is the actual intermediate in the nickel reduction. This points to a certain analogy between chemical nickel plating and catalytic hydrogenation reactions.

Nickel plate deposited with sodium borohydride contains approx. 5 % boron. In the state in which it is deposited the plate is X-ray amorphous and when heat-treated in air at temperatures above 250°C an exothermal, irreversible structural change with separation of nickel boride (Ni₃B) in a softer nickel matrix takes place. The resultant Vickers hardness of approx. 1000 - 1200 kp/mm² is the salient technological property of the nickel boron coats on metal as it means good wear performance and abrasion resistance. When using sodium hypophosphite as the reducing agent phosphorus-containing nickel coatings of similar performance deposit. Compared with such phosphorus-containing metalizing baths NaBH₄ offers the advantage of a much longer life time of the bath which can practically be run without any limit and can be regenerated almost without any limitation. Amine-borane baths, similar to hypophosphite baths, can be operated over a wide pH and temperature range, but preferably at room temperature and in the weakly alkaline range; they also have a very long life time. The high reduction capacity of sodium borohydride and amine-boranes leads only to a small amount of oxidation products, and consequently minimizes the load on the baths.

Amine-borane baths, especially dimethylamine-borane and diethylamine-borane baths, are preferred for the chemical nickel plating of plastics or ceramics. Chemical nickel plating has become successfully established in a wide range of application because the chemically deposited nickel plate is in all cases more resistant than the electrolytically deposited plate of equal thickness. Steels of widely differing composition, aluminium and aluminium alloys, magnesium, magnesium alloys, titanium, molybdenum and tungsten, and also plastics, especially ABS, are chemically nickel plated after the substrates have been thoroughly cleaned and activated. To allow chemical nickel plating of plastics surfaces Pd nuclei are first deposited on these to act as catalysts during the nickel plating.

SUMMARY

Since the revolutionary work by A. Stock and associates more than 5 decades ago and by H.I. Schlesinger and H.C. Brown in the forties sodium borohydride and its derivatives have not only met with wide theoretical and scientific interest and widened our knowledge in many fields of inorganic and organic chemistry but have also secured for themselves a firm position in commercial chemistry. Industrial development is far from complete and it is to be assumed that in future these products will play an even more important role than today.

REFERENCES

1. R.Thompson, Pure Appl.Chem.39(1974)547-559.
2. Anonymous, The WallStreet Journal, April 8, 1976.
3. Anonymous, Japan Chemical Week, No.831, 1.4.1976.
4. H.Niederprüm in Ullmanns Enzyklopädie, 4th Edition, 8(1974)650.
5. H.J.Sanders, Chemical & Engineering News, 1972, 29-31.
6. H.J.Schlesinger, H.C.Brown et al., J.Amer.Chem.Soc.75(1953)186.
7. H.C.Brown, J.Organometallic Chem.100(1975)3-15.
8. A.Stock and E.Kuss, Ber.dtsch.Chem.Ges.47(1914)810.
9. C.Campbell, Advances Chem.Series 32(1961)195.
10. H.G.Klein, H.Niederprüm and E.M.Horn, Metalloberfläche 25(1971)2.
11. W.H.Hough and L.J.Edwards, Advances Chem.Series 32(1961)184.
12. R.T.Holzmann, Production of the boranes and related compounds, Academic Press New York and London (1967)251.
13. Anonymous, Chemical Week, October 19(1968)83-92.
14. e.g.Ventron Co.Callery Chem.Co., Aldrich Boranes Inc., Bayer AG.
15. F.Schubert and K.Lang, Angew.Chemie 72(1960)994.
16. J.Plešek and S.Heřmanek, Sodium Hydride, Iliffe Books Ltd., London (1968)p.18.
17. E.R.Winiarczyk, DAS 12 18 413(1959) and DOS 24 29 521(1974), Metal Hydrides Inc./Ventron Co.
18. W.S.Fedor et al., Industrial and Engng.Chem.49(1957)1664.
19. R.Köster, Houben-Weyl, VI/2(1963)199.
20. K.Lang et al., DBP 1053476(1957), DAS 1262981 and 1281412(1964), Bayer AG.
21. C.Harzdorf, H.Niederprüm and H.Odenbach, Z.Naturforsch.25B(1970)6.
22. E.L.Muetterties and H.W.Knoth, Polyhedral Boranes, M.Dekker Inc., New York(1968).
23. V.Pečák and J.Vit, Maschine-Werkzeug 68(1967)36, Verlag Karl IHL, Coburg.
24. V.Pečák, lecture, Achema Frankfurt, June 1970.
25. H.Odenbach, N.Lönhoff and H.Niederprüm, DOS 161 8387(1967), Bayer AG.
26. H.Nöth and H.Beyer, Chem.Ber.93(1960)931.
27. G.E.Ryschkewitsch and J.W.Wiggins, Inorg.Chem.9(1970)314.
28. H.G.Klein and H.Niederprüm, unpublished.
29. E.Schenker, Neuere Methoden der präparativen organischen Chemie, Verlag Chemie Weinheim, Vol.4(1966), p.196-335.
30. H.C.Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca and London (1972), p.209.
31. Information Bulletin Ventron Co.(1970) and Bayer AG (1975, AC 1001^A and 10015).
32. G.Carrara et al., J.Amer.Chem.Soc.76(1954)4391.
33. G.P.Takor, N.Janak and B.C.Subba Rao, Indian J.Chem.3(1965)74.
34. K.J.Niehues, II.Hydridsymposium of Metallgesellschaft AG, Goslar, May 1974, Abstract p.93.
35. H.Niederprüm and P.Voss, DAS 1300539(1962), Bayer AG.
36. H.Nöth, Nachr.Chem.Techn.23(1975)107.
37. H.Öppinger and H.Hoffmann, Ullmanns Enzyklopädie, 4th Edition, Vol.7(1974)683.
38. DAS 1086713(1956), Societa Farmaceutica Italia.
39. Sumitomo Chem.Co., Jap., Patent 4040-222(1974).
40. Information Bulletin Bayer AG: NaBH₄ in der Chemie der Steroide und Naturstoffe, 1964, Nr.A 0019.
41. H.Niederprüm and W.Simmler, Symposium on Organosilicon Chemistry, Prague 1965, Abstract, p.11; see also W.Noll, Chemie und Technologie der Silicone, Verlag Chemie, Weinheim(1968), p.140,151; H.Niederprüm et al., DAS 1195753, 1216873(1964), Bayer AG.
42. H.C.Brown, Hydroboration, W.A.Benjamin, Inc., New York (1962).
43. G.M.L.Cragg, Organoboranes in Organic Synthesis, M.Dekker Inc., New York(1973).
44. M.Grassberger, Organische Borverbindungen, Verlag Chemie, Weinheim (1971).
45. H.C.Brown, Organic Synthesis via Boranes, J.Wiley & Sons, New York (1975).
46. H.C.Brown and B.C.Subba Rao, J.Amer.Chem.Soc.78(1956)2582; *ibid.*5694.
47. H.C.Brown, (*loc.cit.*30), p.5.
48. Anonymous, Chem.Industrie (1976)A 144.
49. H.C.Brown, 164th Meeting, Amer.Chem.Soc., New York (1972).
Div. of Petroleum Chem.: Possibilities for Organoborane Chemistry in the Petrochemical Area.

50. W.Gerrard, *The Organic Chemistry of Boron*, Academic Press, London and New York (1961) p.164.
51. Information Bulletin Bayer AG: Aminborane-Borazene 1967; Information Bulletin Callery Chem.Co.: Amine-Boranes.
52. S.S.White and H.C.Kelly, *J.Amer.Chem.Soc.* 92(1970)4203.
53. S.Matsumura et al., *Tetrahedron Letters* 45(1968)4703-05.
54. T.Goodart, *Paper Age*, April 1972.
55. T.F.Iula, *Process Engineering* (1975)2, p.93 and 123.
56. G.B.Cohen and E.E.Schrier, *J.Agricult.Food Chem.* 23(1975)661.
57. H.Niederprüm, Chemische Vernickelung, *Angew.Chemie* 87(1975)652.
58. K.Lang, *Metalloberfläche* 19(1965)137.
59. K.M.Gorbunowa et al., *J.Electrochem.Soc.* 120(1973)613.
60. M.Lelental, *J.Catalysis* 32(1974)429; *J.Electrochem.Soc.* 120(1973)1650, *ibid.* 122(1975)486.