THE BEHAVIOUR OF SODIUM TETRAHYDRIDOBORATE IN METHANOL AND TETRAHYDROFURAN

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Sodium tetrahydridoborate reacted with methanol with the consecutive formation of a number of intermediates, of which the identified particles were $[BH_3(OCH_3)]^-$ and $[BH(OCH_3)_3]^-$. The final product of the methanolysis was sodium tetramethoxyborate. The reaction was autocatalytic and was further catalysed by traces of heavy metals. Analysis of the reaction product has indicated the procedure for the preparation of sodium hydridotrimethoxyborate and confirmed the assumed disproportionation of this compound in tetrahydrofuran. The polarographic behaviour of sodium tetrahydridoborate and its substitution derivatives in methanol and/or tetrahydrofuran, compared to their homogeneous oxidation by substrates, suggests that the heterogeneous red-ox process can be characterized as transfer of electrons, whereas the homogeneous red-ox process is controlled by a hydride-transfer mechanism.

Alkaline tetrahydridoborates have long found rewarding use as reducing agents in organic[1,2] and inorganic[3,4] chemistry. Compared to lithium tetrahydridoaluminate they have a milder reducing effect on substrates, but a more specific one[5]. In order to direct the reaction to the desired products and higher yields, which is important in view of the price of the agents, it is necessary to know its kinetics and mechanism. There are only a few papers dealing with these problems in the case of inorganic substrates[6]. All of them suggest that apart from the experimental conditions and composition of the solution the reducing power of an alkaline tetrahydridoborate is influenced mainly by the nature of the solvent. Of the interactions with solvents, hydrolysis of tetrahydridoborates[7] has been the most studied one. In many cases the anion $[BH_4]^-$ has been found inactive toward the substrate[8,9]. The effect of water manifests itself by the formation of a number of intermediates of the general formula $[BH_{4-x}(OH)_x]^-$, which are the actual reducing agents.

Although a number of such reductions are conducted in non-aqueous solvents, little information has thus far been advanced on the behaviour tetrahydridoborates in these media[10,11]. The present paper describes the behaviour of sodium tetrahydridoborate in methanol and/or tetrahydrofuran.

EXPERIMENTAL

Chemicals. Methanol was absolutized by the Lund–Bjerrum method[12]. Tetrahydrofuran, A.G., was left standing a week over solid potassium hydroxide, then it was purified for polarography by the ketyl procedure[13]. The principal electrolytes used in the case of methanol were lithium chloride, A.G., (Lachema Brno) and lithium perchlorate. The latter was prepared from lithium carbonate by the action of perchloric acid. The isolated salt was twice crystallized from water and dehydrated by melting. Tetrabutylammonium perchlorate was obtained by reaction of tetrabutyl ammonium iodide with sodium perchlorate[14]. Sodium and lithium tetrahydridoborates were prepared at the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences. The contents of active hydrogen in these preparations were 97—98% w/w. Lithium and sodium methoxides were prepared by dissolving the freshly sliced alkali metals in methanol[15]. Sodium metaborate was obtained by dehydration of its tetrahydrate, prepared from boric acid and sodium hydroxide[16]. Sodium tetramethoxyborate was obtained by complete methanolysis of sodium tetrahydridoborate and isolation of the solid phase. Sodium hydrido-trimethoxyborate was prepared from sodium hydride and trimethyl ester of boric acid[17]. The preparative reactions in tetrahydrofuran were also reproduced[5,18]. The other reagents were A.G. commercial chemicals from Lachema Brno. All the solid substances were dried over phosphorus pentoxide at 70°C under reduced pressure. The contents of active hydrogen were determined volumetrically[19], the alkali metals were quantitated with titration with hydrochloric acid to the methyl orange end point[20]. Boric acid was determined alkalimetrically after an addition of mannitol, the point of equivalence being indicated potentiometrically.

Apparatus. All solutions were handled by the Schlenk type[21] glassware technique, certain operations with the solid phase were carried out in a glove box. The inert gas was argon, which had been purified in the dry state[22] on the BTS catalyst and freed from traces of water by passing over solid potassium hydroxide and phosphorus pentoxide. Prior to use it was saturated by vapour of the chosen solvent.

Polarographic measurements were carried out with a Polarograph PL-60 (Laboratorní přístroje, Prague), whose recorder EZ 4 had a sensitivity of $3·5 . 10^{-10}$ A/cm. The resistance of the electrolytic circuit was compensated for by an electronic IR-compensator from the firm Metroohm. The products of the electrode reactions were followed by Kalousek's switch (manufactured in the Electronic Laboratory of ÚFCHE J. H., ČSAV[23]). Both the polarographic and the kinetic measurements were carried out in a versatile electrochemical cell[24]. The reaction kinetics were measured in mantled vessels, where the temperature was kept constant (± 0.05°C) with the aid of an ultrathermostat U-10 (G.D.R.). The characteristics of the used mercury dropping electrode were: drop time 4·6 s at a mercury head of 50 cm and at the potential of the saturated calomel electrode in 0·1M-KCl. The flow-rate of mercury was 1·07 mg/s. The reference electrode, made in the laboratory[25], was a calomel electrode with a saturated solution of potassium chloride (s.c.e.). The half-wave potentials were corrected for the liquid interphase potential, chromium bis(η--diphenyl) iodide being employed as a reference compound[26]. The auxiliary electrode was the mercury at the bottom of the vessel or a platinum wire. Since platinum is known to affect the hydrolytic rate the auxiliary electrode was a very short one. In the case of the mercury auxiliary electrode even redistilled mercury had to be freed from a trace of water by heating *in vacuo*. In experiments conducted in tetrahydrofuran the mercury used for the working electrode also had to be perfectly freed from moisture.

The infrared spectra were recorded with a Perkin-Elmer apparatus, using the Nujol technique, and with an apparatus Beckman IR 20A in KBr pellets. Powder radiographs were recorded with an apparatus Mikrometa II (Chirana, ČSR) and evaluated in a comparator. The intensities were estimated with the aid of a subjective scale 1 to 10.

RESULTS AND DISCUSSION

The Behaviour of Sodium Tetrahydridoborate in Methanol

The solution exhibited two polarographic waves. The reduction polarographic wave I, $E_{1/2} = 1.96$ V, is ascribed to reduction of sodium cations, the oxidation polarographic wave II, $E_{1/2} = -0.60$ V, to oxidation of tetrahydridoborate anions. The height of wave I did not change with time. The limit diffusion current of wave II was constant for 3 to 10 min (the so-called induction period on wave II). This time was dependent on the composition of the fundamental electrolyte (I, pH), on the solvent employed and on the depolarizer. In the region of potentials of the limit current of wave II the electrode process was controlled by diffusion of the depolarizer $(i_1 \sim \sqrt{h})$. The "logarithmic analysis" indicated an irreversible electrode process, confirmed by detecting its products with the aid of Kalousek's switch. The limit diffusion current was directly proportional to concentration of the depolarizer up to a concentration of 2 mM. At higher concentrations wave II was distorted by an interfering peak; we were unable to observe visually a vortical character of this peak.

Comparison of heights of waves I and II (corrected for a common drop time) reveals that in the course of the two electrode processes the same number of electrons are exchanged. This means that a tetrahydridoborate anion in methanol gets oxidized at the mercury dropping electrode in a one-electron transfer.

After the induction period the limit current of wave II decreased and there appeared another oxidation wave, III, $E_{1/2} = -0.32$ V. The time course of the limit current of this wave had a peak (Fig. 1); the intersection with the t-axis (t_1) corresponded to the induction period on wave II. At the time t_2 (induction period on wave IV) there began to appear another oxidation wave, IV, $E_{1/2} = -0.10$ V, whose time course
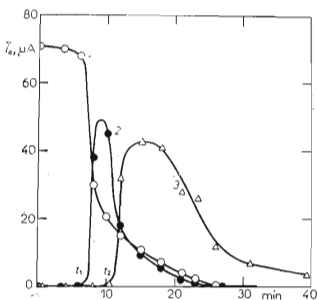

Fig. 1

Time Courses of Limit Currents of Oxidation of Particles on the Mercury Dropping Electrode in a Methanolic Solution of Sodium Tetrahydridoborate

1   $[BH_4]^-$;   2 $[BH_3(OCH_3)]^-$;   3 $[BH(OCH_3)_3]^-$. t_1 and t_2 denote the induction periods on waves II and IV, respectively.

of the limit current also exhibited a maximum. The dependence of the limit currents of waves *III* and *IV* (corrected for the time change) on the height of the mercury level suggests a diffusion character of these waves.

The time course of the limit currents of the oxidation waves *II*, *III* and *IV* (Fig. 1) and their character indicate decomposition of tetrahydridoborate anions *via* two intermediates in a series of consecutive reactions

$$ A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D $$
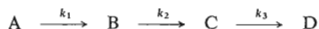
(The depolarizers in the individual waves can be designated: wave *II* $\equiv$ A, wave *III* $\equiv$ B, wave *IV* $\equiv$ C; D is a particle polarographically inactive). The cause of the decomposition of tetrahydridoborate anions is their reaction with the solvent. Since the solvent is present in excess the reaction order is a unit lower. The linear dependence of the natural logarithm of concentration of particles A (after the induction period t_1), B and C (for both at times $t \gg t_{max}$, where t_{max} is the time corresponding to the maximum concentration of an intermediate in the solution) on time demonstrates that the decomposition of particles A obeys a first-order kinetic equation in all the steps. The graphs describing the kinetic course were difficult to reproduce and the rate constants could be determined within an order of magnitude. The gathered experimental evidence suggests that in all probability the reaction is catalysed by traces of transition metals present in the added chemicals. The catalytic effect of salts of transition metals on the decomposition of tetrahydridoborate in aqueous solutions is well known and practically utilized [26-28] The influence of composition of the reaction medium on the rate constants was investigated only qualitatively The rate constants increased with decreasing pH, and decreased with increasing ionic strength. In one series of measurements the rate constants were: $k_1 = 2.49 . 10^{-3} \text{ s}^{-1}$, $k_2 = 4.6 . 10^{-3} \text{ s}^{-1}$, $k_3 = 1.8 . 10^{-3} \text{ s}^{-1}$ (25°C, 0.1M-LiClO$_4$). The induction period t_1 on the time dependence of concentration of particles A suggests that the reaction is a self-catalytic one. The direct reaction of tetrahydridoborate with methanol or with some of its ionized forms is very slow. It is only an intermediate, present in a low concentration, that actually catalyzes the reaction. This is evident from the fact that on the addition of methanolic tetrahydridoborate of an advanced degree of conversion the induction period did not appear. We have not identified the actual catalytic particle since it is impossible to isolate B and C as chemical individua.

The nature of particles in a methanolic solution. In a protogenic medium, free of another oxidating reagent, tetrahydridoborate anions react with the solvent with the consecutive formation of a number of intermediates of the common formula $[BH_{4-x}(OR)_x]^-$, $(OR \equiv OCH_3)$, characterized by a progressive decrease of the number of hydride anions. These are replaced by anions of the solvent molecules, the final

products being molecular hydrogen and tetraanionoborate ions. The possible particles and their characteristics are given in the Table:

Particle	Designation	$E_{1/2}$ V	k, s^{-1}(25°C, $I = 0.1$)
$[BH_4]^-$	A	-0.65	$2.49 \cdot 10^{-3}$
$[BH_3(OCH_3)]^-$	B	-0.32	$4.6 \cdot 10^{-3}$
$[BH_2(OCH_3)_2]^-$	—	—	—
$[BH(OCH_3)_3]^-$	C	-0.19	$1.8 \cdot 10^{-3}$
$[B(OCH_3)_4]^-$	D	$+0.3$	—

In the hydrolysis of sodium tetrahydridoborate only one intermediate was identified[29]. Demonstration of the particle $[BH_3(OCH_3)]^-$ is based on analysis of the kinetics. Particle C was safely identified by the identity of $E_{1/2}$ potentials of the oxidation wave *IV* and the oxidation wave observed in a methanolic solution of $[BH(OCH_3)_3]^-$. Moreover, it is known from the chemistry of lower boranes that a particle of the type $[BH_2(X)_2]$ is extremely unstable[30,31]. If it is produced by methanolysis it immediately undergoes further reaction and its concentration in the solution is below the sensitivity of the analytical method employed. The composition ascribed to par-
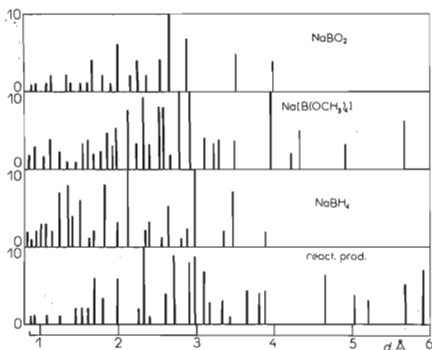

FIG. 2

Comparison of Powder Radiographs
    The reaction product was obtained by the first procedure.

ticle D was derived from a physico-chemical analysis of the solid phase isolated from the solution after methanolysis. Methanolic solutions of this compound exhibit an oxidation polarographic wave of $E_{1/2} \equiv 0.3$ V. This wave can be accounted for by dissolving of mercury, limited by the low solubility of the formed $Hg[B(OCH_3)_4]$.

Sodium hydrido-trimethoxyborate, whose synthesis has been described in the literature, is one of the afore-said intermediates. One preparative procedure is based on the reaction of sodium with trimethyl borate[17]. In another procedure[5,18] the reaction is conducted in tetrahydrofuran. X-ray and IR spectra (Figs 2 and 3), as well as analyses of the solid and the liquid phases, showed that either procedure gave a mixture of compounds, the first affording a better purity of the product desired. Its recrystalization in an aprotic solvent has no purifying effect since it disproportionates[32]: $4 Na[BH(OCH_3)_3] \rightarrow Na[BH_4] + 3 Na[B(OCH_3)_4]$, as has been confirmed by polarography in tetrahydrofuran. This is also the disadvantage of the other preparative procedure. As can be seen from the debyegram of the product obtained by the first procedure (Fig. 2), the strongest lines correspond to $Na[BH_4]$ and $Na[B(OCH_3)_4]$. The presence of $NaBO_2$ can be explained by hydrolysis of the product by aerial humidity. The adsorption bands at 2250 cm^{-1} and 1120 cm^{-1} in the IR spectra of $Na[BH_4]$ and $Na[BH(OCH_3)_3]$ are associated with the B—H
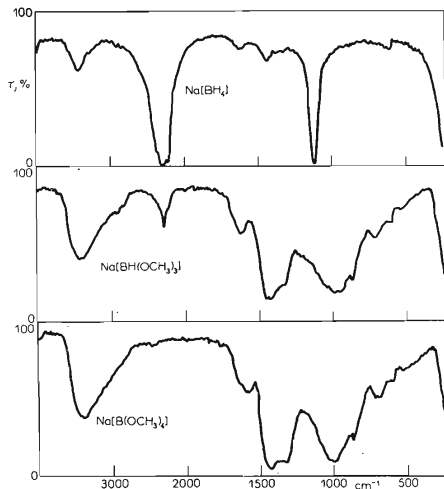
Fig. 3

Infrared Spectra

bonding and the B⟨$\overset{H}{\underset{H}{}}$⟩ deformation vibrations[33]. The band at $3\,500\,cm^{-1}$ in the spectra of all the preparations corresponds to the OH vibrations of water (aerial humidity). In the case of $Na[BH(OCH_3)_3]$ there were also bands at $1\,460\,cm^{-1}$ and $1\,380\,cm^{-1}$ of the deformation symmetrical and asymmetrical vibrations of the CH_3 group, and bands at $2\,950\,cm^{-1}$ and $2\,830\,cm^{-1}$, associated with the vibrations of the methoxy group[34]. The bands at $1\,460\,cm^{-1}$ and $1\,650\,cm^{-1}$ in the spectrum of $Na[BH_4]$ can be accounted for by the presence of methoxyl-containing by-products, which are difficult to remove. The presence of $Na[BH_4]$ in the preparations of $Na[BH(OCH_3)_3]$ has been confirmed polarographically.

The Behaviour of Sodium Tetrahydridoborate in Tetrahydrofuran

In addition to the cathodic wave of $E_{1/2} = -1.85\,V$, corresponding to reduction of sodium cations, the polarogram of sodium tetrahydridoborate in tetrahydrofuran exhibited an oxidation wave of $E_{1/2} = -0.145\,V$ (further referred to as wave E). Experimental data reveal that wave E is a difussive one, associated with an irreversible electrode process ($\alpha = 0.78$). All products of this process were polarographically inactive. Comparison of the limit currents of the two waves leads to the conclusion that the electrode process is associated with the exchange of one electron. The value of $E_{1/2}$ of wave E was markedly dependent on the content of water in tetrahydrofuran. A mere trace of water (comparable to the concentration of the depolarizer) shifted the value of $E_{1/2}$ toward the region of negative potentials and gave rise to a peak of the first type. Direct observation revealed that the peak was of a vortical nature and could not be suppressed by the usual surface-active substances (Triton X-100,
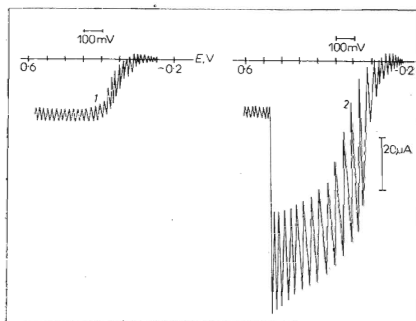

Fig. 4

Polarograms of Sodium Tetra-hydridoborate in Tetrahydrofuran
1 Perfectly dry solvent, *2* moist solvent.

Dowfax 2 Al Powder, polyvinyl alcohol). It was efficiently supressed by eosine. The limit current beyond the peak has the character of a diffusion current and can be used for analytical purposes (Fig. 4). The reaction between methanol and sodium tetrahydridoborate in tetrahydrofuran was practically immediate, the induction period not exceeding 15 s. The reaction led to an equilibrious mixture, the main components having $E_{1/2} = -0.05$ V and $+0.40$ V. The former is ascribed to $[BH_3(OCH_3)]^-$, the latter (hereafter denoted F) has been identified as $[BH(OCH_3)_3]^-$ by the polarographic behaviour of authentic $Na[BH(OCH_3)_3]$.

The Mechanism of Oxidation of Particles $[BH_{4-x}(OR)_x]^-$

The reducing powers of such particles are quantitatively expressed by their $E_{1/2}$, assuming that the overall electrode process of any of them has the same mechanism. The Table shows that the reducing powers of substituted hydridoborates ($R = CH_3$) in methanol are weaker than those of the non-substituted ones. This observation is at variance with the kinetic data, which prove[35] that in homogeneous reductions of a substrate practicles $[BH_{4-x}(OR)_x]^-$ are more reactive with the substrate than $[BH_4]^-$. Consequently, the mechanisms of the homogeneous and the heterogeneous red-ox processes are probably different. With $[BH_4]^-$ in an non-aqueous medium the heterogeneous red-ox process can be characterized as an electron transfer. Unlike their behaviour in water, particles $[BH_4]^-$ in non-aqueous media get oxidized to the corresponding borane by releasing one electron[36]. This primary step, however, is common to either case; $BH_4^- - e \rightarrow BH_4$ (1), $BH_4 \rightarrow BH_3 + H$ (2). In tetrahydrofuran the prevailing next reaction is dimerization of the borane to diborane (3), which proceeds faster than its reaction with the depolarizer (4); the latter, however, can play a significant role in preparative electrolysis: $2 BH_3 \rightarrow B_2H_6$ (3), $BH_3 + BH_4^- \rightarrow B_2H_7^-$ (4). In a protogenic medium, such as methanol, a borane reacts with strong Lewis bases, the formation of intermediates being analogous to that observed in a homogeneous medium. The only polarographically active product of oxidation of $[BH_4]^-$ in methanol is $[BH_3(OCH_3)]^-$. This gets degraded in a series of surface reactions, the final products being $[B(OCH_3)_4]^-$ and molecular hydrogen. The mechanism of the homogeneous red-ox process with $[BH_4]^-$ as the reducing agent can be regarded as a hydride transfer in the primary step. This idea is justified by the fact that $[BH_4]^-$, unlike B_2H_6, attacks molecules in places of their low electron density. Besides, the transfer of a hydride anion from a trialkoxyhydridoborate must be faster than its transfer from a borane, as a stronger Lewis acid. The weaker acidity of $[BH(OCH_3)_3]^-$ results from the simultaneous operation of the inductive effect and the resonance of the methoxy groups.

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