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POLAROGRAPHIC BEHAVIOR OF SODIUM, POTASSIUM, AND LITHIUM BOROHYDRIDES

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Despite the fact that there is an extensive literature on alkali-metal borohydrides [1–5], many of their properties, in particular polarographic ones, have been insufficiently studied. Only two papers have been published on the polarography of borohydrides, and their data are sharply contradictory and very limited, since they concern only one representative of this class of compounds—$NaBH_4$. R. L. Pecsok [6], who studied the oxidation and hydrolysis of sodium borohydride by the polarographic method, found for it (at $pH > 9$) an anodic wave with $E_{1/2} = +0.105 - 0.013\,\mathrm{pH}$, whereas in the earlier work of E. D. Marshall and R. A. Widing [7], $E_{1/2} = -0.6$ V (n.c.e.) was obtained. Pecsok explains this strong discrepancy by the presence of impurities in the preparation available to the preceding authors, although in his own work he used a technical product of about 95% purity. Noting the clearly irreversible nature of the anodic oxidation process of $NaBH_4$, Pecsok nevertheless uses the Ilkovič equation and comes to the conclusion that the reaction proceeds with the participation of eight electrons:

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e.$$

(Figure: Fig. 1. Polarographic curves for $NaBH_4$ in 0.2 M NaOH; lithium borohydride in 0.2 M LiOH; potassium hypoborate in 10% OH; $NaBH(OCH_3)_3$ in 0.2 M NaOH. Axes and annotations include millimeters, potentials −0.4 and −0.8, and concentrations $9.6 \cdot 10^{-3}$, $4.8 \cdot 10^{-3}$, $2.4 \cdot 10^{-3}$, $8 \cdot 10^{-2}$, $4 \cdot 10^{-2}$, $1.6 \cdot 10^{-2}$, and $1 \cdot 10^{-2}$ mol/l.)

Fig. 1

In our laboratory, in the course of work on the application of borohydrides in analytical chemistry [8], a study was undertaken of the polarographic behavior of $NaBH_4$, KBH_4, and $LiBH_4$. For this purpose, both technical preparations ($\sim 80\%$)* and purified preparations, prepared by the method described in [8] and containing more than 98% borohydride, were used.

Polarography was carried out on a Heyrovský micropolarograph, model M-102, with a dropping mercury electrode (capillary constant $K = 3.14^{2/3} \cdot 2.6^{1/6} = 2.50$). In measurements of potentials, a precision voltmeter was used. A careful examination of anodic and cathod-

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* Supplied to us by A. F. Zhigach.

of the entire polarographic curve in the range from +0.2 V to −2.0 V showed that a solution of $NaBH_4$ in NaOH has a single anodic wave with $E_{1/2} = -0.65$ V. This wave decreased with time as the $NaBH_4$ decomposed—and finally disappeared altogether. It also disappeared as a result of destruction of the borohydride by boiling and by acidifying the solution. It is equally well pronounced both in the case of purified $NaBH_4$ and of technical-grade material. The impurities present in the latter, chiefly alcoholate, did not manifest themselves in any way on the polarograms. A specially prepared alcoholate likewise gave no wave. The assignment of the observed wave to the BH_4^- ion was then checked by experiments with purified and unpurified KBH_4 and $LiBH_4$ in KOH and LiOH solutions, respectively. Both of these borohydrides gave the very same wave and behaved polarographically analogously to $NaBH_4$ (Fig. 1, Table 1). The position and character of the wave practically did not change upon variations in the concentrations of the borohydrides or upon changes in the composition of the supporting electrolyte—the introduction of chlorides, etc.

Thus, there remains no doubt that the indicated wave is due to BH_4^- ions and that these ions do not produce any other wave.

The result obtained refutes Pecksok's data. Of the properties of the borohydride wave, we first studied the dependence of its height on the concentration of BH_4^- ions. In the concentration range investigated, 10^{-3} to 10^{-1} mol/L, this dependence is linear. The absence of proportionality between the current and the square root of the effective pressure on the dropping mercury indicates that the limiting current is not entirely diffusion-controlled.

Metal borohydrides in aqueous solutions, especially acidic ones, decompose comparatively rapidly; as a result, polarography under these conditions is extremely difficult. It was precisely for this reason that the working solutions were prepared by us using the corresponding alkalis and alkaline borate buffer mixtures, which simultaneously served as the supporting electrolyte. In choosing the most convenient pH range of the solutions for the work, we made a very important observation. It was found that the height of the borohydride wave at one and the same concentration depends strongly on the pH of the medium. It changes regularly with changing pH, in opposition to the latter. In solutions with sufficiently high pH (above 12.5), in which borohydrides are relatively stable, the wave is practically absent. Hence it logically follows that the observed wave in fact belongs not to the BH_4^- ion, but to some product of its hydrolysis. A number of studies (9–11) have established that hydrolysis of borohydrides proceeds in several stages, at one of which diborane is evolved under certain conditions. The latter, like tetraborane, is capable of reacting with alkalis, forming the so-called hypoborates.

Table 1

	pH	$E_{1/2}$	tg α
$NaBH_4$, $4.8 \cdot 10^{-3}$ mol/L			

pH	$E_{1/2}$	tg α
9.24	−0.636	0.073
9.36	−0.649	0.088
9.50	−0.644	0.077
9.68	−0.658	0.063
9.97	−0.644	0.074
11.07	−0.652	0.065
0.17-0.2 N NaOH	−0.658	0.068
0.17-0.2 N NaOH	−0.650	0.066
KBH_4, $5.7 \cdot 10^{-3}$ mol/L		
10.82	−0.672	0.056
$LiBH_4$, $1 \cdot 10^{-1}$ mol/L		
Aqueous solution after heating to 70°	−0.65	0.063
Potassium hypoborate, $1.5 \cdot 10^{-3}$ mol/L		
10% KOH	−0.664	0.083
$NaBH(OCH_3)_3$, $1.77 \cdot 10^{-2}$ mol/L		
0.2 M NaOH	−0.655	0.059

The work of V. I. Mikheeva and V. Yu. Surs (13) showed experimentally that hypoborates may be regarded as products of individual sta-

···of hydrolysis of borohydrides according to the scheme

$$[BH_4]^- \to [BH_3(OH)]^- \to [BH_2(OH)_2]^- \to [BH(OH)_3]^- \to [B(OH)_4]^-$$

or $BO_2^- \cdot 2H_2O$.

I. Gubo and H. Kalbfass (14), working by the method of infrared spectroscopy, did not find absorption bands that could have been assigned to the ions $BH_2(OH)_2^-$ and $BH(OH)_3^-$, but this does not contradict the scheme given above, since, as the authors themselves note, the "non-observability" of the intermediate products is probably connected with their increased reactivity.

We passed gaseous diborane into concentrated solutions of KOH, NaOH, and LiOH while cooling.* The hypoborate solutions obtained gave, on polarography, one and the same wave with $E_{1/2} = -0.6$ V. Dilution of these solutions led, as in the case of borohydride solutions, to a proportional decrease in the wave height. On standing, the height of the "hypoborate"wave decreases with time, as does the "borohydride" wave, according to a first-order kinetic equation (with respect to hypoborate and borohydride, respectively) (8). The wave practically disappears when the solutions are boiled, and also when they are strongly acidified, owing to decomposition of the hypoborates.

On the basis of the data presented, it is necessary to conclude that the "borohydride" wave is essentially a "hypoborate" wave.

The question of which of the three hypoborates formed during hydrolysis corresponds to the polarographic wave is very difficult to resolve, since it is apparently impossible to have, for experiments, solutions of each of the hypoborates without admixture of the others. Nevertheless, the following considerations may be expressed on this point.

X. V. Shifriny and A. S. Bogonosov, in our laboratory, studied the titration with potassium iodate of solutions of borohydrides and hypoborates in the course of their hydrolysis at room temperature and on heating. It turned out that freshly prepared solutions of lithium borohydride and lithium hypoborate, which, according to the works (11,13), should contain only the first hydrolysis product, $LiBH_3(OH)$, are titrated by iodate but give no polarographic wave. Consequently, the wave cannot belong to the ion $BH_3^-(OH)$. When the indicated solutions are heated to 60° and above, the wave appears, and with further heating of the solutions it persists as long as the titratability of the solutions persists. Since the last titratable product of hydrolysis is the ion $BH(OH)_3^-$, it must be responsible for the polarographic wave. This is confirmed by our experiments with sodium trimethoxyborohydride $NaBH(OCH_3)_3$**, the anion of which, like the ion $BH(OH)_3^-$, contains only one active hydrogen (directly bonded to boron) and gives the same wave with $E_{1/2} = -0.65$ V (Table 1).

The electrode reaction responsible for the observed polarographic wave obviously cannot, contrary to Pecsok, consist in the oxidation of BH_4^- ions with the participation of eight electrons, but must consist in the oxidation of hypoborate ions, for example according to the equation:

$$BH(OH)_3^- + OH^- \rightarrow BO_2^- + 2H_2O + H + e^-$$

or

$$BH(OH)_3^- + 2OH^- \rightarrow BO_2^- \cdot 2H_2O + H_2O + 2e^-.$$

The first of these schemes agrees with the value of the tangent of the slope angle of the plots

$$\frac{i}{i_d - i} = f(E)$$

for borohydrides and hypoborates, close to 0.059 (Table 1), as occurs in reactions involving one electron. In favor of the second scheme are the stoichiometric data of the iodometric titration of $NaBH(OCH_3)_3$ carried out in our laboratory.

* Diborane was obtained by means of an electric discharge by O. I. Rusetskii.
** Provided to us by V. I. Mikheeva and T. N. Dymova.

The kinetics studied by Pecsok by means of the polarographic method essentially pertains not to the reactions of sodium borohydride, but to the hydrolysis and oxidation of intermediate products. But even in this case the results of the study cannot be regarded as reliable, since they were obtained without taking into account the catalytic influence of mercury, which, according to our data, is very considerable.

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