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295 773

JOURNAL OF PHYSICAL CHEMISTRY
(SELECTED ARTICLES)

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UNEDITED ROUGH DRAFT TRANSLATION

JOURNAL OF PHYSICAL CHEMISTRY (SELECTED ARTICLES)

English Pages: 22

SOURCE: Zhurnal Fizicheskoy Khimii, Vol. 36, Nr. 5, 1962,
pp. 989-992, 1089-1094

SOV/76-62-36-5-4/13

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FTD-TT-62-1462/1+2+4

Date 10 Jan. 19 63

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ELECTROSYNTHESIS OF OZONE

V. Ozone Synthesis in a Stream Under Reduced Pressure

V. G. Samoylovich, V. P. Vendillo and
Yu. V. Filippov

Ozone synthesis in an ozonizer is usually carried out at atmospheric pressure or slightly below. Nevertheless, the study of ozone synthesis at reduced pressures is of considerable interest for explaining the kinetics of the formation of ozone.

The formation of ozone at a pressure below atmospheric has been examined in a number of works. According to Warburg [1], over the range from 50 to 200 mm Hg, the yield of ozone with respect to current increases in proportion to pressure. In ozone synthesis from a mixture of gases, the yield of ozone is proportional to the oxygen partial pressure; however, in the case of a mixture of oxygen with nitrogen [2], a higher ozone yield is observed than at the corresponding oxygen partial pressure. According to Hartman [3], the power yield of ozone increases with pressure, while according to another work [4], the ozone yield is highest at 400 mm Hg. The influence of pressure on the

synthesis of ozone has been studied by others [5, 6, 7]. In all these works, the study of ozone synthesis was carried out either under standard conditions, or under certain randomly chosen oxygen flow rates, which makes difficult a kinetic examination of these data. Semiokhin [8] studied the kinetics of ozone synthesis at various pressures, but the basic results were obtained at higher pressures.

Experimental

Standard apparatus [9] was used in this work; at the output of the gas stream was an RVN-20 pump, which created the necessary evacuation. The ozonizer also had the previously described design with a removable inner electrode [10]. The dimensions of the ozonizers are given in Table 1. The series of experiments on various reactors were performed at a constant current: 44.4 ma on reactors 1 and 2 and 30 ma on reactor 3. At a pressure of 760 mm Hg, for reactor 3 the current was 22 ma, since maintaining 30 ma required voltages which were too high. The temperature of the water cooling the electrodes of the ozonizer was 22.5°, and the frequency of the supply voltage was 1250 cps. The oxygen flow rate was varied in each series of experiments from 5 to 500 $\frac{l}{hr}$.



Fig. 1. Dependence of ozone concentration upon the factor $\frac{u}{v}$ for reactor 1: 1) 780 mm Hg; 2) 620 mm Hg; 3) 440 mm Hg; 4) 320 mm Hg; 5) 160 mm Hg.

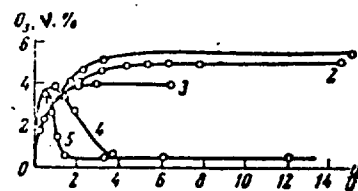


Fig. 2. Dependence of ozone concentration upon the factor $\frac{u}{v}$ for reactor 2: 1) 780 mm Hg; 2) 620 mm Hg; 3) 440 mm Hg; 4) 320 mm Hg; 5) 160 mm Hg.

The results of experiments at 160, 320, 440, 620 and 780 mm Hg in ozonizers 1, 2 and 3 are shown in Figs. 1, 2, and 3 (respectively). The ozone yield in volume per cent. is plotted on the y-axis, and the factor $\frac{u}{V}$ on the x-axis. (Values of $\frac{u}{V}$ were calculated for the volumetric rate of the gas at a given pressure.)

Results

A distinctive feature of the kinetic curves of ozone synthesis at reduced pressures is the presence of maxima at a certain value of the factor $\frac{u}{V}$, which are more sharply expressed the lower the pressure. Although they give curves with maxima, the kinetic equations of successive chemical reactions cannot be used to explain these maxima, since in the case under consideration the decomposition of the intermediate product (after which ozone could be taken) leads not to the disappearance of the starting substance, but to its restoration. It can be assumed that these maxima are caused by processes in the formation or decomposition of ozone, which are distinguished by a different development in time or which are functions of the gas flow rate in a different way. The decomposition of ozone outside the reactor - which occurs either dispersedly in space or on the surface of the input and output tubes, or at definite places in the apparatus (e.g., in the absorbers, in the heaters, etc.) - is naturally taken as one of these processes. This decomposition goes on after the reactor as well as before it. In the latter case transfer of ozone from the reactor occurs owing to counter-current diffusion.

The general case of the kinetics of ozone synthesis taking into account the diffusion removal of ozone from the reactor and its decomposition by concentrated "negative sources" has been examined in an

earlier work [11].

Table 1

Reactor	Diameter, mm		Discharge gap, mm	Ozonizer diameter	Length of reaction zone, mm
	Inner electrode	Outer electrode			
1	23	24	0.5	35	250
	20	24	2.0	35	250
	16	24	4.0	35	250

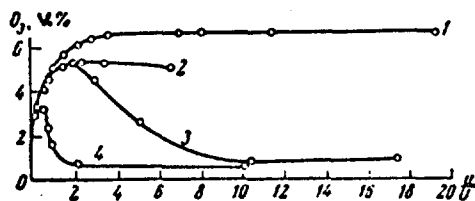


Fig. 3. Dependence of ozone concentration upon the factor $\frac{u}{v}$ for reactor 3: 1) 620 mm Hg; 2) 440 mm Hg; 3) 320 mm Hg; 4) 160 mm Hg.

In this case the maxima on the kinetic curves can appear due to the competition between mass and diffusion flow at the input to the reactor. However, the maxima on the kinetic curves can also appear due to ozone decomposition after the reactor in the gas-outlet tubes and in the pipette for sampling the gas. This corresponds to dispersed ozone decomposition outside the reactor. The solution of the general differential kinetic equation in this case is similar to the solution in the case of concentrated sources of decomposition. However, in general, the differential equations are very complicated, and calculation of experimental data by them is difficult. Let us examine the particular limiting cases of the general problem. The first of these

includes the assumption of an ideal mixing in the reactor and concentrated sources of ozone decomposition before the reactor [11]. In this case the maxima on the kinetic curves must be observed at one and the same values of $P \cdot V_{\max}$ (see Table 2).

Table 2

Pressure, mm Hg	Rate, $\frac{1}{\text{hr}} V_{\max}$			$P \cdot V_{\max} \cdot 10^{-3}$		
	Reactor			Reactor		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
780	16	—	—	12.5	—	—
620	18	—	—	11.5	—	—
440	28	49	—	12.3	21.5	—
320	40	76	192	12.8	24.3	61.4
160	85	171	380	13.6	27.2	61.0

The second particular limiting case includes the assumption of ideal displacement in and beyond the reactor. The ozone concentration at the input to the reactor is zero and counter-current diffusion does not occur. Let us examine ozone decomposition after the reactor, which we shall consider a 1-st order reaction, i.e.,

$$\frac{dx}{dt} = -k_1' x, \quad (1)$$

where x is the ozone concentration, t time, and k_1' the decomposition constant of ozone after the reactor. Hence

$$x = x_0 e^{-k_1' t}, \quad (2)$$

where x_0 is the initial ozone concentration.

In a flow system, in the case of ideal displacement, we can replace time t by the ratio of the volume of the system after the reactor F_k to the volumetric flow rate V , and take as the initial concentration the concentration at the output of the reactor

$$x = x_0 e^{-k_1' F/V} \quad (3)$$

In the case of ideal displacement in question, the ozone concentration at the output of the reactor will be determined by the equation [12]

$$x_0 = \frac{k_0}{k_1} (1 - e^{-k_1 \cdot \frac{u}{V}}), \quad (4)$$

where k_0 is the ozone formation constant, k_1 the decomposition constant of ozone in the reactor, and u is the active power. Substituting the value of x_0 from Eq. (4) into Eq. (3), we obtain

$$x = \frac{k_0}{k_1} (1 - e^{-k_1 \cdot \frac{u}{V}}) \cdot e^{-k_1 F/V}. \quad (5)$$

This equation can correspond to kinetic curves with maxima since the first and second derivatives of x with respect to $\frac{1}{V}$ have a real value; the second derivative is negative. From the condition

$$\frac{dx}{d(\frac{1}{V})} = 0 \text{ we find}$$

$$e^{-k_1 \frac{u}{V_{\max}}} = 1 + \frac{k_1}{k_1'} \cdot \frac{u}{F}, \quad (6)$$

or

$$V_{\max} = \frac{k_1 u}{\ln(1 + \frac{k_1 u}{k_1' F})} \quad (7)$$

For simplicity, especially at low values of $k_1 \frac{u}{V}$, we can expand $e^{k_1 \cdot \frac{u}{V}}$ into a series and limit it to the two first terms of the expansion. Then we find that

$$V_{\max} = k_1' F. \quad (8)$$

If it is assumed that k_1 is inversely proportional to pressure, which, in particular, can hold in diffusion decomposition of ozone after the reactor, we find that

$$V_{\max} P = \text{const.} \quad (9)$$

As indicated above, this dependence was observed experimentally. Thus decomposition after the reactor in the case of ideal displacement

can also explain the appearance of maxima on the kinetic curves. In fact, in ozone synthesis in an ozonizer an intermediate case between ideal displacement and ideal mixing is observed [12], therefore, both these processes play a role.

Conclusions

1. The kinetics of ozone synthesis in a stream at reduced pressure was studied. The kinetic curves in this case have an anomalous form with maxima.

2. An explanation of this form of the kinetic curves was proposed which takes into account ozone decomposition outside the reactor. If ozone decomposition occurs before the reactor, then the maxima on the kinetic curves are the result of competition between the mass and counter diffusion flows. The difference between the dependences of ozone formation in the reactor and decomposition after the reactor can be a cause of the maxima in ozone decomposition after the reactor.

M. V. Lomonosov Moscow State University Submitted July 20, 1960.

REFERENCES

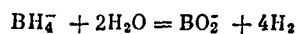
1. E. Warburg. Ann. physic, 28, 17, 1929.
2. E. Warburg. Z. phys., 32, 245, 1925.
3. E. Hartman. Trans. Amer. Electrochem. Soc., 44, 54, 235, 1923.
4. Soc. anon l'Azote Francais. Brit., 140, 777, Mar. 22, 1920.
5. E. Briner. Helv. chim. acta, 13, 678, 1930.
6. E. Briner. Bull. Soc. chim. belges, 62, No. 12, 55, 1953.
7. J. C. Davins. J. Electrochem. Soc., 103, 460, 1956.
8. I. A. Semiokhin, Dissertation, Moscow, 1951.

9. V. P. Vendillo, Yu. M. Yemel'yanov and Yu. F. Filippov.
Zavodsk. laboratoriya, 25, 1401, 1959.
10. Yu. V. Filippov and V. P. Vendillo. Zh. fiz. khimii, 33,
2358, 1959.
11. Yu. V. Filippov. Vestn. Mosk. un-ta, No. 4, 153, 1959.
12. Yu. V. Filippov and Yu. M. Yemel'yanov. Zh. fiz. khimii,
35, 407, 1961.

POLAROGRAPHIC STUDY OF BOROHYDRIDES OF ALKALI METALS

K. N. Mochalov and G. G. Gil'manshin

A polarographic study of the alkali borohydrides LiBH_4 , NaBH_4 , KBH_4 , and CsBH_4 because of the widening application of these new, highly active compounds, is of considerable interest, particularly for ascertaining the states in which they are found in aqueous solutions. Under these conditions the borohydride anion undergoes fairly rapid hydrolysis, according to the scheme



or



The mechanism and intermediate steps in this complicated process have not yet been established with certainty.

Only two papers (in addition to the papers by the authors of the present article) relating to the polarography of borohydrides are known. These papers, which deal with NaBH_4 , contradict each other sharply. In one of them [1] it was established that the half-wave potential was equal to -0.6 v (saturated calomel electrode). In the other [2] it was found for sodium borohydride at $\text{pH} > 9$ that the anode wave has a value of $E_{1/2} = +0.105 - 0.013 \text{ pH}$. In our previous article [3] a

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criticism of the data found in Ref. [2] was given, while in Refs. [4, 5] the kinetics of the hydrolysis of NaBH_4 and KBH_4 were studied chemically. In this article we have presented the results of further polarographic investigation of alkali borohydrides in an aqueous medium.

Experimental Section

The polarographic measurements were performed on a type 7-77-46 ("Orion," Hungary) automatic recording polarograph with a dropping mercury electrode, with a capillary constant $K = 3.97^{2/3}$, $2.44^{1/6} = 2.90$. The reference electrode was a drainable saturated calomel electrode. Technically prepared borohydrides (80%), as well as borohydride purified by the method described in Ref. [6] and containing more than 98% borohydride, were used for the work. The content of the basic component was determined by iodate titration [7].

In order to avoid the decomposition of NaBH_4 , KBH_4 , and LiBH_4 , the solutions were prepared by dissolving weight samples in 0.2 M solutions of sodium, potassium, and lithium alkali, respectively, since at this alkali concentration the borohydrides are sufficiently stable. The polarography was carried out with various supporting electrolytes — in 0.2 M alkali solutions and in borate and phosphate buffer solutions. But in the alkali and borate buffer solutions the polarographic waves were most clearly pronounced.

Careful examination of the interval of polarization between +0.2 and -2.0 v (s.c.e.) showed the presence of one and the same identical anode wave with the potential $E_{1/2} = 0.65$ v (s.c.e.) at room temperature in the case of NaBH_4 , KBH_4 , and LiBH_4 in the above-mentioned solutions. This agrees well with Ref. [1] and contradicts Ref. [2]. In order to test the assumption that this wave is due to impurities

[2], comparative polarography was carried out on solutions of technical and purified sodium and potassium borohydrides. The polarographic wave was displayed equally well in all cases, regardless of the presence of impurities. The impurities present in the technical borohydride [20%], chiefly alcoholate, as well as specially synthesized sodium alcoholate, did not show up on the polarization curves. The observed polarographic wave diminished in the course of time, until it disappeared completely, as the borohydride decomposed. The same effect was caused by the decomposition of borohydride by the addition of acid and by heating. The position and character of the waves remained practically unchanged during a change in the borohydride concentration and during changes in the composition of the supporting electrolyte brought about by the introduction of various amounts of chlorides and other compounds.

All this indicates that the observed polarographic wave with $E_{1/2} = 0.65$ v (s.c.e.) really caused by the borohydride ion BH_4^- and that these ions give rise to no other wave. As for the Pecsok wave with $E_{1/2} = +0.105 - 0.013$ pH, it was not found by us. But, as is well known, even at these electrode potentials mercury dissolves at the anode in alkaline or weakly alkaline solutions. The anode current caused by this is usually so great (of the order of tens of μa) that the Pecsok borohydride wave cannot be observed under these conditions.

Polarization curves recorded by us for one and the same supporting electrolyte in the presence, as well as the absence, of borohydride proved to be identical. From these curves it can also be clearly seen that the presence of borohydride has no noticeable effect on the wave resulting from the dissolution of mercury. Consequently, the wave observed in Ref. [2] could have been caused only by mercury

dissolving at the anode. In light of the facts just mentioned, doubt arises with regard to the proportionality noted in Ref. [2] between the height of the borohydride wave and the borohydride concentration.

Characteristics of the Borohydride Wave. In order to determine the nature of the anode current caused by BH_4^- ions, we studied the dependence of the limiting current value on the height of the mercury column. The variability of the quantity K in the equation $i = K \sqrt{H_{\text{Hg}}}$ gives us the right to conclude that the current is not entirely diffusion current. Experiments conducted at 15, 25, and 35° have shown that at each of these temperatures a change in the pH of the medium does not affect the half-wave potential, and it even remains practically constant during a change in temperature in the interval from 15 to 35°.

In order to study the height of the polarographic wave as a function of the concentration of borohydrides, the previously prepared solutions were diluted to the desired extent immediately before each experiment and subjected to polarography. The diluting was done with alkali solutions calculated in such a way that the pH was kept constant in all cases. The pH values were determined with a reading accuracy of 0.001 pH. Glass electrodes, made from a special glass which permitted accurate measurements in the high pH region, served as the indicator electrodes. The dependence of the height of the NaBH_4 waves on the concentration of the BH_4^- ions in the interval between $1 \cdot 10^{-3}$ and $1 \cdot 10^{-4}$ moles/liter proved to be linear.

The necessity of maintaining a constant pH in these experiments follows from an important observation made by us, namely, that the height of the wave of one and the same borohydride solution varies regularly with the pH and antibatically to it (Fig. 1). This dependence has not yet been noted in the literature. In strongly alkaline

solutions in which the borohydrides are sufficiently stable, the polarographic wave is very small and often practically absent. But it appears immediately upon acidification of these solutions, i.e., during the incipient hydrolysis of the BH_4^- ions, and is due therefore to the formation of intermediate reaction products.

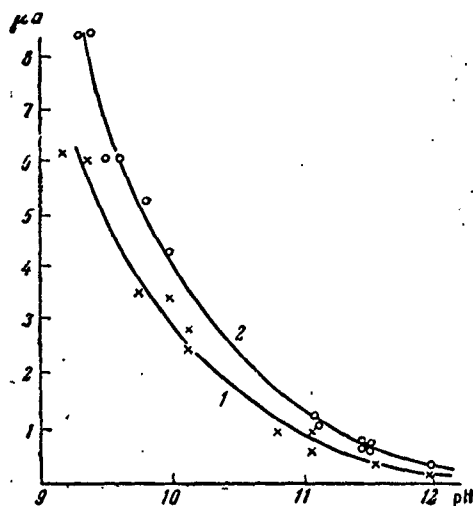


Fig. 1. Dependence of the height of potassium and sodium borohydride waves on pH: 1) $[\text{KBH}_4] = 0.0104$ moles/liter $t = 13.3^\circ$; 2) $[\text{NaBH}_4] = 0.1064$ moles/liter, $t = 15.6^\circ$.

We have also obtained data pertaining to the dependence of the wave height on the temperature for constant pH. In this case, the electrolytic cell was located in a glass jacket through which water circulated at a set constant temperature. The polarographic waves for both borohydrides increased with temperature. This, it must be assumed, occurs not only as a result of an increase in the ionic mobility, but also as a result of

a speeding up of the hydrolysis.

Origin of the Polarographic Wave. Since the origin of the polarographic wave, as was stated above, is related to the hydrolysis of BH_4^- ions, it is extremely interesting to observe the change in the wave height with time. This change reflects the kinetics of the over-all process of formation and decomposition of the intermediate product which gives rise to the polarographic wave. The solutions for these experiments were prepared from pure NaBH_4 and KBH_4 in solvents, the temperature of which had been preset, and were placed in a thermostat with deviations of not more than $\pm 0.1^\circ$. Individual portions of

the solution were subjected to polarographic analysis at the same temperatures within strictly measured time intervals. Iodate titration and pH measurement were performed simultaneously. Certain data characterizing the change in wave height with time for borate buffer solutions are given in Table 1.

TABLE 1

Variation in the Height of the Polarographic Wave of Borohydrides with Time in Borate Buffer Solutions

[NaBH ₄] ₀ =2,3·10 ⁻² , pH=10,06; 15°		[NaBH ₄] ₀ =2,4·10 ⁻² , pH=10,47; 15°		[KBH ₄] ₀ =2·10 ⁻² , pH=10,17; 15°		[NaBH ₄] ₀ =1,6·10 ⁻² , pH=10,50; 25°	
time, min.	μa	time, min.	μa	time, min.	μa	time, min.	μa
0	—	0	—	0	—	0	—
3	8,60	4	4,00	15	7,2	4	5,2
8	12,60	11	8,50	19	10,00	9	11,6
12	14,80	18	11,00	29	13,00	14	14,20
16	15,40	29	13,40	38	13,60	20	15,60
23	15,40	33	13,90	48	14,00	25	16,00
28	15,20	55	14,40	74	12,80	30	16,20
46	14,60	76	13,80	144	10,52	44	15,60
105	11,60	91	13,20	207	9,20	65	15,20
131	10,60	211	11,80	264	8,10	115	13,20
189	9,36	340	10,70	360	6,60	216	10,00
251	6,00	453	9,60	459	5,20	352	7,20
309	5,40	—	—	—	—	440	5,40
418	4,28	—	—	—	—	544	4,90
515	3,24	—	—	—	—	—	—

The same picture was observed in all experiments performed. At first the height of the polarographic wave (expressed in μa) increases and then, after passing through a maximum, decreases regularly. The position and height of the maxima, as can be clearly seen from Table 1, depend greatly on the temperature and pH of the medium.

Analysis of the experimental data leads to the conclusion that the higher the temperature and the lower the pH, i.e., the higher the rate of hydrolysis of the BH₄⁻ ions, the more rapidly the maximum is attained. After it is reached, a regular drop occurs, until the polarographic wave disappears completely. The data from the iodate

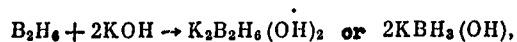
titration show that on the downward segments of the curves the regular decrease in the height of the wave is in strict conformity with the concentration of borohydride present, as determined by iodate titration. In this case a linear dependence between the wave height and the borohydride concentration is observed, as can be seen in Fig. 2. The dependence of the wave height on the pH at 15°C is shown in Figs. 3 and 4 for three different concentrations of NaBH₄ ($1.0 \cdot 10^{-2}$, $1.2 \cdot 10^{-2}$ and $1.4 \cdot 10^{-2}$ moles/liter), as well as its dependence on the temperature for the same three concentrations with the pH equal to 9.59 and 10.03. As can be seen from Fig. 3, the dependence of the wave height on the pH is distinctly curvilinear in nature. The change in height is independent of the borohydride concentration in a given solution. The graphs in Fig. 4 allow us to judge the effect of the temperature and the pH on the wave height.

Discussion of Results

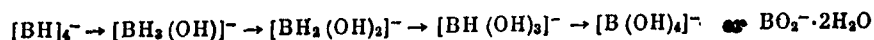
A number of investigations [8, 9, and 10] have established the fact that the hydrolysis of BH₄⁻ ions proceeds in several stages, in one of which diborane B₂H₆ may be produced under certain conditions. Its formation is due to the tendency of BH₄⁻ ions to go to BH₃ + H⁻ under the action of the electrical fields of the cations [11]. Therefore it may be assumed that the appearance of a polarographic wave in solutions of borohydrides is caused by one of these products. In order to verify this, experiments involving the polarography of solutions of calcium hydride and diborane were carried out. However, when calcium hydride was introduced into the various buffer solutions and into the alkali solutions the polarographic wave did not appear. It was also absent when diborane was passed through water, pyridine, or water-pyridine mixtures. But when diborane (diluted with hydrogen) was

passed through cooled NaOH and KOH solutions, a wave with $E_{1/2} = -0.65$ v, generated in this case by hypoborates [12] being formed in the solution, invariably appeared. The height of this wave decreased in proportion to the diluteness of the solutions. It also decreased with time, like the height of the "borohydride" wave, according to a first-order kinetic equation (for hypoborate and borohydride, respectively). The wave disappeared almost completely, when the solutions were boiled, or when they were acidified as a result of decomposition of the hypoborates.

The hypoborates, which are formed in the reaction between diborane and the alkali solutions, such as



may be considered as the products of the individual stages of the hydrolysis of borohydride



according to Ref. [12].

By considering together 1) the fact established by us that the wave is not attributable to BH_4^- ions, but to the products of their hydrolysis, 2) the scheme of the hydrolysis of BH_4^- ions with the formation of hypoborates, 3) the existence of a wave for the hypoborates, which is identical in potential and characteristics to the borohydride wave, we are forced to conclude that the "borohydride" wave is, in reality, a "hypoborate" wave. Although it is difficult to answer the question of exactly which of the three hypoborate ions, formed consecutively in the course of the hydrolysis, is responsible for the observed wave, a certain singularity in the hydrolysis of $LiBH_4$, and also a study of the polarographic behavior of certain borohydride derivatives, particularly sodium trimethoxyborohydride, may prove to

be of considerable assistance in clarifying it.

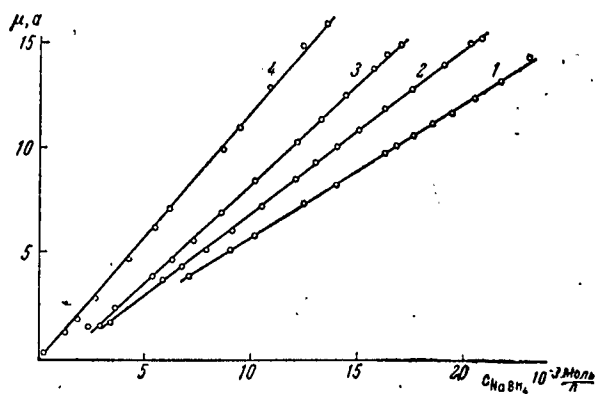


Fig. 2. Height of the NaBH_4 wave as a function of its concentration and pH at $t = 15^\circ$: 1) pH = 10.49; 2) pH = 10.055; 3) pH = 9.958; 4) pH = 9.062.

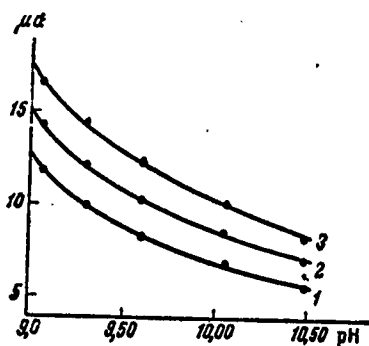


Fig. 3. The dependence of the height of the NaBH_4 wave on the pH of the solution at 15° : 1) $[\text{NaBH}_4] = 1.0 \cdot 10^{-2}$ moles/liter; 2) $[\text{NaBH}_4] = 1.2 \cdot 10^{-2}$ moles/liter; 3) $[\text{NaBH}_4] = 1.4 \cdot 10^{-2}$ moles/liter.

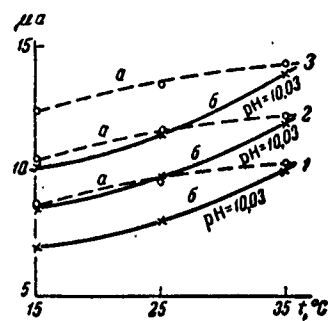


Fig. 4. Dependence of the height of the NaBH_4 wave on the temperature at pH = 9.59 (curves a) and 10.03 (curves b) for concentration of NaBH_4 : 1) $1.0 \cdot 10^{-2}$ moles/liter; 2) $1.2 \cdot 10^{-2}$ moles/liter; 3) $1.4 \cdot 10^{-2}$ mole/liter.

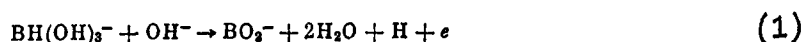
According to V. I. Mikheyeva and Ye. I. Fedneva [10], the hydrolysis of LiBH_4 at 20°C is confined to its conversion to the first hypoborate $\text{LiBH}_4(\text{OH})$. Conversion to subsequent products occurs only with heating. Taking this observation into account a carefully cooled moderately alkaline solution of LiBH_4 was prepared. This solution displayed no wave when subjected to polarography under ordinary conditions. Hence it follows that the wave cannot be attributed to $\text{BH}_3(\text{OH})^-$ ions. When this solution was heated to 60° , a wave appeared having all the characteristics mentioned above and continued to remain as long as active hydrogen, titratable by iodate, remained in solution. On the other hand, sodium trimethoxyborohydride $\text{NaBH}(\text{OCH}_3)_3^*$ gives the same wave with $E_{1/2} = -0.65 \text{ v (s.c.e.)}$, which shows up very clearly in a medium so strongly alkaline that borohydrides show no wave at all in it, on account of the almost total absence of hydrolysis.

Since $\text{NaBH}(\text{OCH}_3)_3$ contains one active hydrogen (bonded to boron), it is extremely likely that the carrier of the polarographic wave in borohydride solutions is hypoborate, which also has one active hydrogen, i.e., the last titratable product of the hydrolysis — $\text{BH}(\text{OH})_3^-$ ions. It should be noted, however, that in a study of the solid products of the hydrolysis by infrared spectroscopy [13] no absorption bands which could have been ascribed to $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ were observed. But, as was noted in Ref. [13], the absence of these bands may be due to the increased activity of these products.

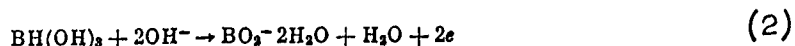
Certain comparative characteristics of the polarographic wave of the compounds studied by us are given in Table 2. The electrode

* Furnished us by V. I. Mikheyeva and T. N. Dymova.

reaction giving rise to the observed polarographic wave cannot, notwithstanding Pecsok's data, consist of the electrochemical oxidation of BH_4^- ions in which eight electrons take part, but must consist of the oxidation of $\text{BH}(\text{OH})_3^-$ ions according to the scheme



or



The first of these schemes is in good agreement with the slope of

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

for borohydrides and hypoborates, which is close to 0.059 (Table 2), as it should be in reactions in which one electron takes part. The second scheme is in good agreement with the stoichiometric data obtained by Kh. V. Shifrin and A. S. Bogonostsev, who studied the iodate titration of sodium trimethoxyborohydride.

TABLE 2
Comparative Characteristics of the Polarographic Wave of
a Number of Compounds

Test product	Concentration, moles/liter	pH of test solution	$E_{1/2}$, v SoSeSo	$\tan \alpha$
NaBH ₄	4,8·10 ⁻³	9,24	-0,64	0,073
	4,8·10 ⁻³	9,97	-0,64	0,074
	4,8·10 ⁻³	11,07	-0,65	0,065
	4,8·10 ⁻³	0,17-0,2 M NaOH	-0,65	0,067
KBH ₄	5,7·10 ⁻³	10,82	-0,67	0,056
CsBH ₄	5·10 ⁻³	Borate buffer solution pH = 10,03	-0,66	0,060
LiBH ₄	1·10 ⁻¹	Aqueous solution after heating 70°	-0,65	0,063
Calcium hypoborate	1,5·10 ⁻³	10% solution of KOH	-0,66	0,083
NaBH(OCH ₃) ₃	1,77·10 ⁻²	0,2 M	-0,65	0,059

Conclusions

1. The contradiction existing in the literature regarding the half-wave potential of sodium borohydride has been resolved. It has been established that NaBH_4 , KBH_4 , LiBH_4 and CsBH_4 give rise to one and the same anode wave with the potential $E_{1/2} = -0.65 \text{ v (s.c.e.)}$. A change in the pH of the medium and in the temperature between 15 and 35° has no marked affect on the value of the potential.

2. The height of the wave depends greatly on the pH and varies antipatically with it. At $\text{pH} > 12.5$, i.e., under conditions when, practically speaking, no hydrolysis of BH_4^- ions is taking place, there is no polarographic wave. The wave arises under the action of factors which cause and accelerate the hydrolysis (acidification, heating, catalysis).

3. It has been experimentally demonstrated that the "borohydride" wave on the volt-ampere curve is attributable not to the BH_4^- ion, but to one of the products of its hydrolysis, presumably the $\text{BH}(\text{OH})_3^-$ ion, and is therefore actually a ("hypoborate" wave).

4. The nature of the kinetic curves, polarographically recorded for NaBH_4 and KBH_4 , shows that the hydrolysis of these compounds proceeds in accordance with the theory of the kinetics of consecutive reactions.

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Received August 19, 1961

REFERENCES

1. E. D. Marschall, and R. A. Widing. Atomic. Energy, Commission Document, 2914 cited in No. 2, June, 1950.
2. R. L. Pecsok. J. Amer. Chem. Soc., 75, 2862, 1953.
3. K. N. Mochalov and G. G. Gil'manshin. Reports Acad. Sci. USSR, 132, 134, 1960.

FTD-TT-62-1462/1+2+4

4. K. N. Mochalov, Kh. V. Shifrin, and A. S. Bogonostsev. Trans. of the Kazan Chemical-Technological Institute, No. 26, 135, 1959.
5. K. N. Mochalov, Kh. V. Shifrin, and A. S. Bogonostsev. Zhurnal fizicheskoy khimii (in press).
6. K. N. Mochalov, Kh. V. Shifrin, and A. S. Bogonostsev. Trans. of the Kazan Chemical-Technological Institute, No. 26, 140, 1959.
7. D. A. Lyttle a. ath., Analyt. Chem., 24, 1843, 1952.
8. H. Y. Schlesinger and A. B. Burg. J. Amer. Chem. Soc., 62, 3429, 1940.
9. M. Kilpatrick, and C. D. McKinney. J. Amer. Chem. Soc., 72, 5474, 1950.
10. V. I. Mikheyeva, and Ye. I. Fedneva. Reports Acad. Sci. USSR, 101, 99, 1955.
11. F. G. Stone. Quart. Rev., 9, 199, 1955.
12. V. I. Mikheyeva and V. Yu. Surs. Reports Akad. Sci. USSR, 93, 67, 1953.
13. G. Goubeau, H. Kallfass. Z. anorg. und allgem. Chem., 299, 167, 1959.