Polarographic Investigation of Unsubstituted Benzohydroxamic Chlorides

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The polarographic reduction of benzohydroxamic chloride and *p*-chlorobenzohydroxamic chloride was investigated and the currents found were compared to the currents of benzaldoxime and *p*-chlorobenzaldoxime.

Experimental

Benzohydroxamic chloride was prepared by chlorination of benzaldoxime in etheric solution at laboratory temperature using elementary chlor [1]. The starting benzaldoxime as well as *p*-chlorobenzohydroxamic chloride were prepared according to literature [2, 3]. The starting *p*-chlorobenzaldoxime was prepared from *p*-chlorobenzaldehyde (Loba — Chemie) according to [4].

Polarographic study of substances

The ethanolic 1×10^{-3} M solutions of substances were subject to polarographic investigation. Before measurement the solutions were mixed with equal volume of buffer solution and after removing oxygen by means of nitrogen the recording of current-voltage curves was made using a Kalousek vessel with separated saturated calomel electrode. After this recording, the pH of solutions was measured with a laboratory PHK-1 pH-meter with glass electrode (Beckman E 102). A polarograph LP-60 (Laboratory Instruments) was used for polarographic investigation. The switched curves were recorded by means of a commutator described before [5].

Benzohydroxamic chloride was studied polarographically both in sulfuric acid of different concentrations and in Clark—Lubs or Britton—Robinson buffer solutions.

It was found that the substance was reduced in 5 M-H_2SO_4 giving a diffusion wave the limiting current (i_3) of which was proportional to the concentration of depolarizer and to the square root of the height of mercury reservoir. At H_2SO_4 concentrations ranging from 1 M to 0.1 M this wave splits into two waves; the first is so indistinct that it is not possible to determine either its half-wave potential or current. The height of this indistinct wave does not practically change with sulfuric acid concentration. The current sum of both split waves depends only slightly on the concentration of acid and practically equals the original limiting current of non-split wave (i_3). In Clark—Lubs buffer solution at about pH 1.5 only one wave was found the height of which corresponded to the height of wave in 5 M-H_2SO_4.

The authors are aware that the interpretation of polarographic data obtained in 5 M-H_2SO_4 is questionable (presence of impurities, *etc.*); nevertheless the data thus ob-

Table 1

Half-wave potentials and currents of the waves of benzohydroxamic chloride and benzaldoxime

Benzohydroxamic chloride							Benzaldoxime			
medium − pH	$i_1 \times 10^{-3}$ [A]	$-E_{1/2}$ [V]	$i_2 \times 10^{-6}$ [A]	$-E_{1/2}$ [V]	$i_3 \times 10^{-6}$ [A]	$-E_{1/2}$ [V]	medium − pH	$i \times 10^{-6}$ [A]	$i \times 10^{-6}$ [A] (gelatine)	$-E_{1/2}$ [V]
5 M-H$_2$SO$_4$					6.2	0.75	5 M-H$_2$SO$_4$	7.8	5.2	0.66
1 M-H$_2$SO$_4$					6.0	0.93	1 M-H$_2$SO$_4$	6.9	5.0	0.70
0.5 M-H$_2$SO$_4$					6.0	0.95	0.5 M-H$_2$SO$_4$	5.6	5.2	0.73
0.1 M-H$_2$SO$_4$					6.0	1.00	0.1 M-H$_2$SO$_4$	6.1	5.4	0.77
C.−L. 0.97					5.9	0.95	C.−L. 0.97	6.4	0	0.84
B.−R. 2.22			1.0	0.84	2.4	1.15	B.−R. 2.22	6.6		0.90
B.−R. 2.97	1.0	0.20	1.5	0.89	1.1	1.23	B.−R. 2.97	7.0		0.91
B.−R. 3.45	1.6	0.22	5.0	1.00						
B.−R. 3.60	2.5	0.27	5.1	1.02			B.−R. 3.96	7.2		0.98
B.−R. 4.30	3.7	0.28	3.1	1.02						
B.−R. 4.75	3.7	0.29	2.0	1.03			B.−R. 4.79	6.5		0.995
B.−R. 4.90	3.7	0.29	1.6	1.02						
B.−R. 5.34	4.1	0.31	1.1	1.02						
B.−R. 5.67	3.7	0.32	1.0	4.55			B.−R. 5.75	6.5		1.05
B.−R. 6.40	3.8	0.32					B.−R. 6.28	6.3		1.10
B.−R. 6.50	3.8	0.34								
B.−R. 6.91	3.7	0.36					B.−R. 7:02	6.3		1.09
B.−R. 8.02	3.8	0.40					B.−R. 0.36	6.2		1.15
B.−R. 9.46	3.8	0.47					B.−R. 9.78	5.3		1.18
B.−R. 10.75	3.7	0.53					B.−R. 10.60	3.8		1.19
B.−R. 12.38	3.6	1.24					B.−R. 12.38	0.6		1.22

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tained are quite in agreement with other particulars and enable us to interpret the corresponding polarographic curves. A considerable temporal dependence of all currents obtained was found in Britton—Robinson buffer solutions over the pH range from 2 to 12. At pH 2.22 a rather indistinct wave with limiting current i_1 was found at positive potentials. This wave was followed by the second wave with limiting current i_2 which by and by turned into the third wave with limiting current i_3. These three waves were also obtained
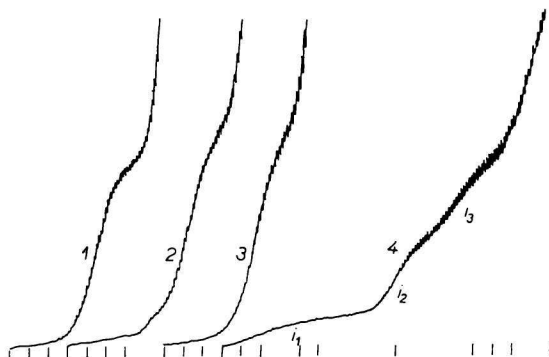

Fig. 1. Polarographic curves of benzohydroxamic chloride.
1. from -0.3 V (SCE) in 5 M-H_2SO_4; 2. from -0.4 V (SCE) in 1 M-H_2SO_4; 3. from -0.5 V (SCE) in Clark—Lubs buffer at pH 0.87; 4. from 0.0 V (SCE) in Britton—Robinson buffer at pH 2.97.
Concentration of depolarizer 5×10^{-4} M; sensitivity 1 : 500, 100 mV/absc., drop time 3.1 sec.
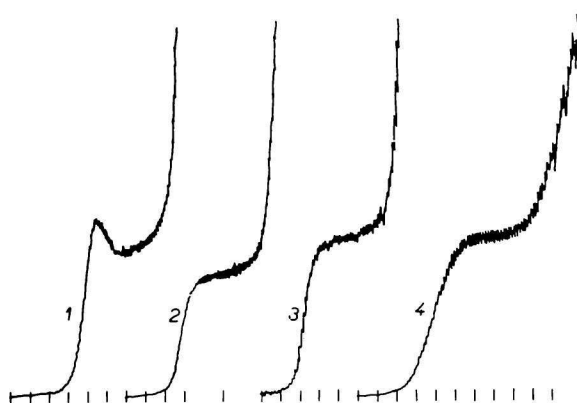

Fig. 2. Polarographic curves of benzaldoxime.
1. from 0.3 V (SCE) in 2 M-H_2SO_4 (without gelatine); 2. from -0.4 V (SCE) in 1 M-H_2SO_4 (with gelatine); 3. from -0.4 V (SCE) in Clark—Lubs buffer at pH 0.97; 4. from -0.5 V (SCE) in Britton—Robinson buffer at pH 2.97.
Concentration of depolarizer 5×10^{-4} M; sensitivity 1 : 500, 100 mV/absc., drop time 3.1 sec.

Table 2

Half-wave potentials and currents of the waves of p-chlorobenzohydroxamic chloride and p-chlorobenzaldoxime

	p-Chlorobenzohydroxamic chloride						p-Chlorobenzaldoxime		
medium − pH	$i_1 \times 10^{-6}$ [A]	$-E_{1/2}$ [V]	$i_2 \times 10^{-6}$ [A]	$-E_{1/2}$ [V]	$i_3 \times 10^{-6}$ [A]	$-E_{1/2}$ [V]	medium − pH	$i \times 10^{-6}$ [A]	$-E_{1/2}$ [V]
5 M-H_2SO_4					6.9	0.91			
1 M-H_2SO_4					6.6	0.95			
0.1 M-H_2SO_4					5.5	1.08			
C. — L. 0.97					6.0	0.91	C. — L. 0.72		0.71
B. — R. 2.22	0.73	0.11	1.6	0.78	1.7	1.08	B. — R. 2.22	6.4	0.86
B. — R. 3.36	1.3	0.12	4.6	0.92			B. — R. 3.98	6.0	1.0
B. — R. 4.58	2.7	0.17	2.6	0.94			B. — R. 4.78	6.0	1.09
B. — R. 5.30	2.8	0.20	0.9	0.97			B. — R. 5.75	5.6	1.13
B. — R. 6.23	2.8	0.24					B. — R. 6.28	3.5	1.16
B. — R. 7.02	2.8	0.28					B. — R. 7.02	1.5	1.18
B. — R. 7.66	2.7	0.29					B. — R. 7.60	0.77	1.19
B. — R. 8.12	2.8	0.34							
B. — R. 9.17	2.8	0.40							
B. — R. 9.48	2.8	0.41							
B. — R. 10.69	2.8	0.45							
B. — R. 10.72	2.8	0.45							
B. — R. 12.33	0.5	0.53							

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at pH 2.97 at which the temporal variation of all three waves was followed. In the first 10 minutes the first and the second wave (i_1 and i_2) increased while the third wave (i_3) disappeared. Then the values of limiting currents i_1 and i_2 remained constant for about 50 minutes, but after three hours a distinct downward tendency was observed in both waves. Only the first two waves were recorded in buffer solution at pH 3.45. These waves were observed up to pH 6. Merely the first wave (i_1) was observed in neutral or alkaline medium. The values of limiting current of this wave depend on time in alkaline medium (pH 12.38), where the current i_1 falls to a half of its original value in about 70 minutes.

The character of electrode process was examined by means of Kalousek commutator with an auxiliary shunt voltage in 5 M-H_2SO_4 ($E_a = -1.0$ V), in 1 M-H_2SO_4 ($E_a = -1.1$ V), in Clark—Lubs buffer solution at pH 0.97 ($E_a = -1.1$ V), and in Britton—Robinson buffer solutions at pH 2.22 ($E_a = -1.4$ V), pH 2.97 ($E_a = -1.4$ V), pH 3.45 ($E_a = -1.4$ V), pH 3.60 ($E_a = -1.4$ V), and pH 5.67 ($E_a = -1.4$ V) using the circuit (I) according to [6]. In all these cases a full irreversibility of polarographic reduction was ascertained.

To interpret the benzohydroxamic chloride reduction, the curves of benzaldoxime were recorded in the whole pH range under analogous conditions. In sulfuric acid medium the reduction waves of benzaldoxime were covered with a maximum which, however, could be suppressed by gelatine.
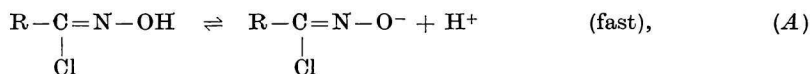
The half-wave potentials of individual waves of benzohydroxamic chloride and benzaldoxime found as well as correspondent currents are given in Table 1 and plotted in Figs. 1 and 2. In Table 1 the values of current of benzaldoxime including maxima in sulfuric acid and the values of current after suppressing the maxima by gelatine are presented separately. The values of current of benzohydroxamic chloride in sulfuric acid are overall values of current including the first little distinct wave. In all cases the values of current are read in half-wave point. A smaller sum of the currents thus obtained when compared with the sum of all currents observed may be due to errors in reading for which the poorly readable waves (i_2 and i_3) are responsible.
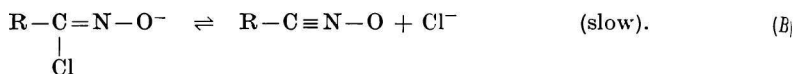
The polarographic study of p-chlorobenzohydroxamic chloride leads to a similar conclusion. In this case the wave (i_3) was also found in the medium of 1 M-H_2SO_4. This wave was indistinctly split into two waves which could not be read off reliably. In Britton—Robinson buffer solution three waves (i_1, i_2, i_3) were found at pH 2.22. On the other hand, only two waves (i_1, i_2) were found in the pH range from 3.6 to 5.3 while only a single wave i_1 appeared in neutral or alkaline region. The diffusion character of waves was proved in 1 M-H_2SO_4 and Britton—Robinson buffer solution at pH 3.36.

In order to verify the polarographic reduction of this substance, p-chlorobenzaldoxime was studied polarographically under equal conditions. The values of half-wave potentials and currents found are given in Table 2 where the overall values of limiting currents (i_3) are also included.

Discussion

The polarographic reduction of benzohydroxamic chloride and p-chlorobenzohydroxamic chloride is complicated by dissociation reactions [7, 9] which have been verified potentiometrically

$$R-\underset{\underset{Cl}{|}}{C}=N-OH \;\rightleftharpoons\; R-\underset{\underset{Cl}{|}}{C}=N-O^- + H^+ \qquad \text{(fast)}, \qquad (A)$$

$$R-C=N-O^- \quad \rightleftharpoons \quad R-C \equiv N-O + Cl^- \qquad \text{(slow)}. \qquad (B)$$
$$\underset{\overset{|}{Cl}}{}$$

In view of the value of dissociation constant it may be assumed that the undissociated form prevails in the medium of mineral acids where it is reduced giving a diffusion wave (i_3). The splitting of this wave is due to the effect of sulfuric acid while it does not appear in the medium of perchloric acid. The verification of the six-electron reduction described in literature [7, 8] failed because of considerable instability of the substance as well as of the fact that the fundamental conditions for the application of macroreduction were not fulfilled (equal shape of curves for dropping and surface mercury electrode and time constancy of half-wave potentials of the curve for large-surface electrode).

In the pH range between 2 and 3 a hydrolysis of benzohydroxamic chloride to nitrile oxide occurs. The rate of this hydrolysis is comparable with the time of polarographic recording. The increase in concentration of nitrile oxide corresponds to the increase in current of the waves i_1 and i_2 under simultaneous decrease in the current i_3 which corresponds to the reduction of benzohydroxamic chloride. In this case our results are in agreement with [7, 8] although the authors cited do not mention the third wave.

In medium with pH exceeding 3 the rate of benzohydroxamic chloride hydrolysis is greater than the rate of polarographic recording. For this reason, only the waves i_1 and i_2 were recorded. The wave i_1 is a two-electron wave and the relationship between its half-wave potential and pH is rather complicated. At pH 3 the shape and half-wave potential of the wave i_2 conform to those of the wave of benzaldoxime. Hence, the two-electron reduction of benzonitrile oxide i_1 may be expressed by equation

$$R-C \equiv N-O + 2H^+ + 2e \quad \rightarrow \quad R-CH=NOH. \qquad (C)$$

This process is followed by a four-electron reduction of aldoxime in the wave i_2

$$(R-CH=NOH)\,H^+ + 4e + 3H^+ \quad \rightarrow \quad R-CH_2-NH_2 + H_2O \qquad (D)$$
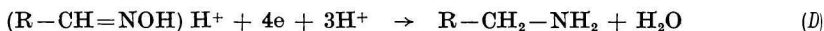
for in agreement with [10] nitrile may be expected to be the product of nitrile oxide reduction. Since the wave i_2 does not reach the current values of benzaldoxime wave and decreases with increasing pH much more rapidly than the benzaldoxime wave, it may be concluded that there are two reaction mechanisms effective and that one of them corresponds to equation (C).

In quite an analogous way p-chlorobenzohydroxamic chloride is reduced. In the presence of mineral acids the wave i_3 corresponding to the reduction of p-chlorobenzohydroxamic chloride has been found. In Britton—Robinson buffer solution at pH 2—3, p-chlorobenzohydroxamic chloride which is reduced in the wave i_3 as well as its hydrolysis products, i.e. p-chlorobenzonitrile oxide reducible in the waves i_1 and i_2 exist. The shape and half-wave potential of the waves i_2 corresponded well to the waves of p-chlorobenzaldoxime but the current i_2 decreased with increasing pH still more divergently than the current of p-chlorobenzaldoxime. Hence it may be concluded that the polarographic reduction of p-chlorobenzonitrile oxide may be expressed by equations (C) and (D) with limitations analogous to those which have been pointed out for the reduction of benzonitrile oxide. The time instability of the substance does not, unfortunately, allow a more detailed study of this reduction by means of a large-surface electrode.

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