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# Polarographic Study of Some Benzhydrazides

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Fig. 1. Beginning of the curve from 0.0 V; 240 mV/div. Polarrecord B-261, metrohm

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## Abstract

## Full Text

## Chemistry

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# Polarographic Study of Some Benzhydrazides

*(Presented by Academician A. E. Arbuzov, October 17, 1963)*

Recently, in a paper by one of us and R. Kalvoda <sup>(1)</sup>, it was shown that in acidic solutions with  $\text{pH} < 4.0$ , benzamide is reduced at a dropping mercury electrode at the discharge potentials of hydrogen ions by a two-electron mechanism, with formation of benzaldehyde ammonia. Owing to its instability, the latter decomposes into benzaldehyde and benzaldehyde imine, which appear on the oscillographic curves  $dE/dt = f(E)$  as artifacts.

In the present work we set forth the results of a study of the mechanism of reduction of benzhydrazide and *n*-nitrobenzhydrazide. Benzhydrazide on polarograms of solutions with  $\text{pH} 2.8-7$  gives reduction waves, the limiting current of which almost merges with the background discharge current. Under these conditions, *n*-nitrobenzhydrazide, in addition to the waves corresponding to reduction of the nitro group, also gives a wave before the background. As can be seen from Fig. 1, which gives the polarogram of a solution of *n*-nitrobenzhydrazide with  $\text{pH} 3.47$ , the height of the reduction wave at negative potentials is almost two times smaller than the height of the four-electron wave of reduction of the nitro group. The height of the benzhydrazide wave is likewise almost two times smaller than the height of the four-electron wave of the nitro group. To elucidate the mechanism of the two-electron reduction of benzhydrazide, an oscillopolarographic study was carried out of its solutions with  $\text{pH}$  from 2 to 7.

**Fig. 1.** Beginning of the curve from 0.0 V; 240 mV/div. Polarrecord B-261, metrohm

Oscillograms  $dE/dt = f(E)$  of acidic solutions of benzhydrazide, in addition to the main notch near the right-hand extreme point of the curve, corresponding to its polarographic wave, contain two more distinct notches and one small notch between them (curve *a* in Fig. 2), which are kinetic in character. These notches belong to artifacts—intermediate products formed as a result of reduction of benzhydrazide. When the constant component of the current is decreased so

Fig. 2. Oscillopolarographic curves  $dE/dt = f(E)$  of benzhydrazide solutions: a, b with pH 2.0; c -pH 6.25

Figure 2: Fig. 2. Oscillopolarographic curves  $dE/dt = f(E)$  of benzhydrazide solutions: a, b with pH 2.0; c -pH 6.25

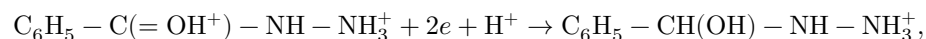
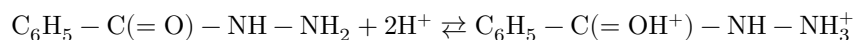
that reduction of benzhydrazide does not occur, the artifact notches disappear. When small amounts of benzaldehyde are added to a solution with pH 2.0, an increase is observed in the depth of notches 2 and 3 (curve *b* in Fig. 2), with the depth of notch 2 continuing to increase for some time. The depth of notch 1 increases somewhat upon addition of small amounts of hydrazine to the solution. Additional measurement of the positions of the notches of benzaldehyde and benzoylhydrazone of benzaldehyde on the curves  $dE/dt = f(E)$  of solutions of these compounds with pH 2.0, and comparison of the results obtained with the data for benzhydrazide, showed that notch 3 on the benzhydrazide curve corresponds exactly to benzaldehyde, while the small notch 2 corresponds to its benzoylhydrazone.

For peak 1, good agreement was found with the peak of benzaldehyde hydrazone. As the pH of the solution increases, the artifact peaks on the curves  $dE/dt = f(E)$  of benzhydrazide solutions become more distinct, and the depth of peak 2 increases relative to the depths of peaks 1 and 3. In the region of pH about 8, the artifact peaks are practically poorly distinguishable.

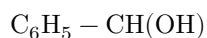
The observed picture of the oscillopolarographic behavior of benzhydrazide resembles the behavior of benzamide<sup>(1)</sup>. The difference is that the artifact peaks in the case of benzhydrazide are observed at higher pH values of the solution.

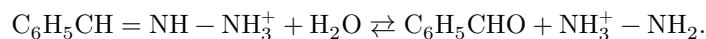
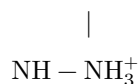
Fig. 2. Oscillopolarographic curves  $dE/dt = f(E)$  of benzhydrazide solutions: a, b with pH 2.0; c -pH 6.25

Apparently, as a result of the two-electron reduction of benzhydrazide, proceeding according to the scheme



benzaldehyde hydrazine is formed, which, as a result of dehydration, is converted into benzaldehyde hydrazone, and, upon cleavage of a hydrazine molecule, gives benzaldehyde





On classical polarograms these compounds cannot appear, since, having formed in the near-electrode space during the lifetime of one drop, they would immediately react electrochemically on the surface of the electrode at the reduction potential of benzhydrazide. However, on oscillograms the formation of benzaldehyde and its hydrazone, controlled by the rate of decomposition of benzaldehyde hydrazine, is observed distinctly—they correspond to peaks 3 and 1. Under these conditions, apparently, benzaldehyde partially has time to react with benzhydrazide with the formation of benzaldehyde benzoylhydrazone, to which peak 2 on the curves  $dE/dt = f(E)$  corresponds. Analogously to benzhydrazide, the hydrazide group in *p*-nitrobenzhydrazide behaves under electrochemical reduction at the dropping mercury electrode. It may be assumed that during the two-electron reduction of benzhydrazide there occurs either cleavage of the single nitrogen–nitrogen bond with formation of benzamide and ammonia, as proposed by Lund <sup>(2)</sup> in the case of isonicotinoylhydrazine, or cleavage of the single carbon–nitrogen bond with formation of hydrazine and benzaldehyde. However, such an assumption is eliminated, since in the first case there re-

...the oscillographic behavior of benzhydrazide would remain unexplained, while in the second case the reduction wave of benzhydrazide would be a four-electron one. In addition, it is necessary to take into account the fact that at  $\text{pH} > 4.0$  benzamide is not reduced polarographically and, consequently, the observed notches of artifacts on the curves  $dE/dt = f(E)$  of benzhydrazide cannot be attributed to products formed as a result of the electroreduction of benzamide.

The formation of benzaldehyde and its hydrazone during decomposition of the reduction product of benzhydrazide can be detected if the polarogram is recorded with the aid of the Kalousek switch.

A polarogram obtained with the Kalousek switch at an auxiliary potential at which benzhydrazide is not reduced corresponds to the background curve (Fig. 3, curve 1). However, if an auxiliary potential at which reduction of benzhydrazide occurs is applied to the dropping mercury electrode, the polarogram obtained in this case contains two steps. These steps, in their potentials, approximately correspond to the reduction waves of benzaldehyde hydrazone and benzaldehyde (Fig. 3, curve 2). It should be noted that the wave heights of the latter compounds decrease somewhat as the switching frequency is increased. This phenomenon is probably associated with accumulation of the decomposition products of benzaldehyde hydrazine on the electrode surface: the lower the switching frequency, the larger the amount of benzaldehyde and its hydrazone

Fig. 3. Polarograms of a benzhydrazide solution at pH 6.85, recorded with the Kalousek switch; 1—auxiliary potential, 1.7 V; 2—auxiliary potential,  $-2.2$  V; switching frequency 25 Hz; Polarecord E-261, metrohm

Figure 3: Fig. 3. Polarograms of a benzhydrazide solution at pH 6.85, recorded with the Kalousek switch; 1—auxiliary potential, 1.7 V; 2—auxiliary potential,  $-2.2$  V; switching frequency 25 Hz; Polarecord E-261, metrohm

that is formed during this decomposition in the interval between two successive switchings of the electrode potential.

**Fig. 3.** Polarograms of a benzhydrazide solution at pH 6.85, recorded with the Kalousek switch; 1—auxiliary potential, 1.7 V; 2—auxiliary potential,  $-2.2$  V; switching frequency 25 Hz; Polarecord E-261, metrohm.

It appears that, for the first time, we have succeeded in following, with the aid of the Kalousek switch, the formation of intermediate products during reduction which exhibit cathodic behavior.

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1. R. Kalvoda, G. Budnikov, *Coll. Czechoslov. Chem. Commun.*, **28**, 838 (1963).
2. H. Lund, *Acta chem. scand.*, **17**, 1077 (1963).

*Note: Figure translations are in progress. See original paper for figures.*

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