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THE ELECTROCHEMICAL REDUCTION OF 2-NITROBUTANOL(1)

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Polarographic investigations of some aliphatic nitro compounds[1-5] reported up till now point to the fact that the reduction of the nitro group in these compounds stops definitely at the corresponding hydroxylamines giving a four-electron reduction wave. The electrochemical reduction of 2-nitrobutanol(1) can, however, lead also to the formation of 2-aminobutanol(1)[6], but the mechanism of this reduction has not been theoretically explained. In our work the electrochemical behaviour of 2-nitrobutanol(1) was investigated with purpose to explain the mechanism of the electrochemical reduction of this compound in 2-aminobutanol(1).

The polarographic behaviour of 2-nitrobutanol(1) was investigated in a wide range of pH values of solutions (2,0 - 10,5). Britton-Robinson buffers, prepared according to literature,[7] were used as the supporting electrolytes. A well-defined polarographic wave was obtained, whose half-wave potential was shifted towards more negative values with the increase of pH. In acid media the limiting current was constant and independent of the pH change, whereas in the alkaline it decreased abruptly with the increase of pH values. Measurements of the dependence of the limiting current on the depolarizer concentration, the height of the mercury column, as well as temperature coefficients and the logarithmic analysis show that the polarographic wave of 2-nitrobutanol(1) in acid media is irreversible, but it has a diffusion character. By comparison of the height of the polarographic wave of 2-nitrobutanol(1) with the height of the depolarizer wave with a given number of electrons (maleic acid, n=2)[2] it was established that four electrons take part in the polarographic reduction of 2-nitrobutanol(1) in acid media, this corresponding to the reduction to 2-hydroxylaminobutanol(1). All these results indicate that the polarographic behaviour of 2-nitrobutanol(1) is very similar to the behaviour of other aliphatic nitro compounds.

On the basis of polarographic data electroreductions of 2-nitrobutanol(1) were performed at a controlled potential on the plateau of the polarographic wave (-0,85 V vs. S.C.E.) using mercury pool cathode. The influence of temperature (25-70°C) and medium (Britton-Robinson buffer, pH=2,00, 10% hydrochloric acid) on the course of electroreduction was investigated by recording absorption curves in the ultraviolet region as well as by recording polarograms in fixed time intervals (every 30 minutes) after the beginning of the reaction. The content of 2-aminobutanol(1) in the catholyte was determined by means of Leeds and Smith's method[8], and it was found to be present only in small quantities, dependent on reduction conditions. The follow up of the electroreduction by measuring absorption curves in the ultraviolet region points also to a dependence of the reduction course on conditions under which it is performed (temperature and medium).

Some representative results of the electroreduction of 2-nitrobutanol(1) on the mercury pool cathode are given in the following table:

t°C	Medium	% of 2-aminobutanol(1) in catholyte	Quantity of current Asec	n
25	Britton-Robinson buffer, pH=2,00	1,9	6600	3,70
70	Britton-Robinson buffer, pH=2,00	2,4	6180	3,50
25	10% HCl	8,2	7560	4,20

The results quoted above point to the positive influence of temperature increase and, particulary, of the presence of hydrochloric acid on the rise of the 2-aminobutanol(1) content. During the electroreductions at lower temperatures formation and accumulation of an unidentified substance absorbing intensively in UV-region with a maximum at 270 nm was observed also. This absorption maximum subsides in intensity as the reduction proceeds.

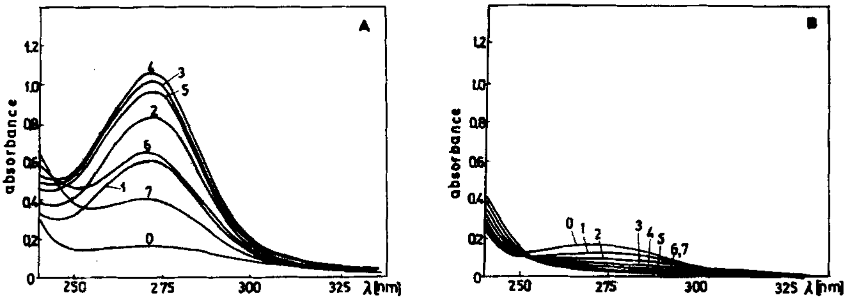
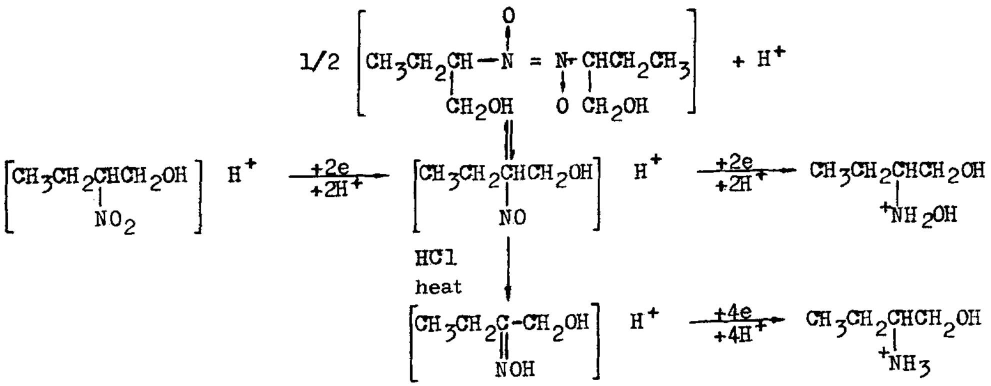


Fig.1. UV-spectra drawn out during electroreduction of 2-nitrobutanol(1) in Britton-Robinson buffer, pH=2,00. Sample 0 was taken before the beginning of electrolysis, sample 1 thirty minutes afterwards, sample 2 after sixty min., etc. Temperature of solution 25°C (A) and 70°C (B).

Taking in consideration theoretical reflexions of Collin and coworkers[9], it can be concluded that the above mentioned substance (max. 270 nm) corresponds to the dimer of 2-nitrosobutanol(1), which is in equilibrium with the corresponding mono-nitroso compound, this equilibrium depending highly on temperature.

On the basis of the results of our own investigations as well as on the basis of literature data[9,1o] the following scheme of the mechanism of electroreduction of 2-nitrobutanol(1) in acid media can be suggested:



Under given optimal reaction conditions (increased temperature, presence of hydrochloric acid) the electroreduction proceeds in a six-electron process over the corresponding nitroso and oxime steps ending with 2-aminobutanol(1) as final product, whereas the electroreduction at lower temperatures in absence of a strong acid (HCl) leads over the nitroso step to the formation of 2-hydroxylaminobutanol(1) in a four-electron process. On the other hand, there probably exists an equilibrium between the mono-nitroso compound and its dimer, and this is not electroreducible. This equilibrium depends highly on temperature and it is shifted at lower temperatures in the direction of nitroso dimer formation.

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