Polarographic Determination of Nitroalditols in Decomposition Mixtures with Hydrogen Peroxide

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The presented polarographic study on a series of selected D- and L-forms of 1-deoxy-1-nitroalditols was aimed to elaborate an analytical method for their determination in pure state and particularly in decomposition mixtures with hydrogen peroxide. This method is convenient for kinetic purposes and also to monitor the important stage of nitromethane syntheses of saccharides, their purity and stability. Addition of 10 % platinum on charcoal suppresses the H_2O_2 waves; presence of catalytic amounts of molybdate ions does not disturb determination at optimal conditions: at pH 8 and 20 °C.

Nitroalditols, the meaningful intermediates of one of the fundamental synthetic methods for extending the saccharide carbon chain (the nitromethane synthesis [1]) are prepared by a base-catalyzed addition of nitromethane to aldoses [2]. Salts of stereomeric nitroalditols formed in this way are separated by fractional crystallization [3], so that a pure nitroalditol isomer can be used for the next synthetic step. Nitroalditols are then decomposed by mineral acids – application of the Nef reaction [4] – or by oxidative degradation giving rise to a higher aldose. Molybdate ions-catalyzed decomposition of 1-deoxy-1-nitroalditols with hydrogen peroxide (effect of peroxomolybdic acid) was found quite successful [5].

Nitroalditols as nitro compounds [6], H_2O_2 and Mo(VI) compounds as constituents of redox systems are active polarographically. Nitroalditols reveal two separate cathodic waves in aqueous media. The wave at more positive potentials corresponds to a four-electron reduction of the nitro group to a hydroxylamine derivative, whilst that at more negative potentials to a two-electron reduction of the hydroxylamino group to an amine. Hydrogen peroxide undergoes reduction to water showing a two-electron wave merging with the more positive one of nitroalditols. Appropriately chosen experimental conditions for nitroalditols can prevent interactions with the Mo-catalyst and possibly also with aldoses [7] being formed. Polarographic waves due to H_2O_2 can be suppressed by its decomposition [8].

Goal of this paper was to elaborate a method for determination of both the pure 1-deoxy-1-nitroalditols and their mixtures with H_2O_2 and Mo(VI) ions based on the study of their polarographic behaviour. Such method has to be simple and rapid, making it possible to obtain data for kinetic studies of decompositions and also for monitoring the course of syntheses.

EXPERIMENTAL

The commercial 1-deoxy-1-nitroalditols were purified by paper chromatography on Whatman No. 3 sheets, with butanol—ethanol—water ($\varphi_r = 5\!:\!4\!:\!1$) as the elution system and the solution of $AgNO_3$ and NaOH in water—ethanol as the visualization reagent. Chemicals for preparation of buffer solutions were of anal. grade and the pH values of buffers were adjusted against Titrisol (Merck) standards. Hydrogen peroxide, its decomposition catalysts, and ammonium molybdate were of the highest purity available (Aldrich).

Polarographic measurements were performed on a Universal Polarograph OH 105 instrument (Radelkis, Budapest). Measurements of pH were performed on Standard pH-meter PHM 82 (Radiometer, Copenhagen), in a thermostated universal vessel EA 880 using glass electrode EA 109U and reference electrode (SCE) of the type EA 404 (all from Metrohm, Herisau). The temperature was maintained with accuracy $\pm$ 0.1 °C by the help of U 1 thermostat (Prüfgeräte Medingen, Dresden).

The polarographic study was based on recording the dependences of polarographic current i_D on concentration c of nitroalditols [$i_D = f_1(c)$] – calibration plots, the relationship between polarographic current and temperature [$i_D = f_2(T)$], the square root of the mercury reservoir height $h^{1/2}$ [$i_D = f_3(h^{1/2})$] of the dropping electrode, and acidity of solutions under investigation [$i_D = f_4(pH)$]. Solutions were measured in a closed thermostated H-shaped vessel (working compartment) with a sintered glass filter and a saturated calomel electrode (SCE), separated by a salt bridge. Optimal working conditions were found as follows: the concentration of nitroalditols $c = 5 \times 10^{-4}$ mol dm^{-3}, the mercury reservoir height $h = 49$ cm,

temperature $(20 \pm 0.1)\,°C$, sensitivity $s = 1.6 \times 10^{-7}$ A, recorded from -0.4 V *vs.* SCE to more negative values of the potential. The parameter of dependences f_1 to f_4 varied in the following intervals: concentrations of nitroalditols 5×10^{-5}—10^{-3} mol dm^{-3}, temperature 15—60 °C, $h^{1/2} = 5$—9 cm$^{1/2}$, pH 4.0—10.2. Acetate, phosphate, carbonate, and ammonium fundamental buffers were used to adjust the pH values of solutions polarographed. The optimal medium was found to be the phosphate pH 8 $(0.1 \text{ mol dm}^{-3})$ buffer.

The 10 cm^3 samples of nitroalditols were polarographed in aqueous buffer solutions after removal of oxygen by a stream of bulb nitrogen. Comparable amount of H_2O_2 $(5 \times 10^{-4} \text{ mol dm}^{-3})$ and a catalytical amount of ammonium molybdate (0.003 mass %) were added to the model mixtures of nitroalditols in order to trace suppression of the H_2O_2 polarographic wave at varying amounts of different catalysts of H_2O_2 decomposition (Pd—C, Pt—C, MnO$_2$, and Ag$_2$O) at various time intervals. Larger amounts of H_2O_2 (three times of eqv.) were also tested.

RESULTS

The polarographic behaviour of a complete series of nitrohexitols, nitropentitol, and nitroheptitol was investigated to see the influence not only of the structure, but also of the C-chain length. Concordant results were obtained with all nitroalditols when estimating diffusion character of the polarographic current (f_2 and f_3). The correlation coefficient value $r > 0.999$ was found for the dependence $i_D = f(h^{1/2})$. The value for temperature coefficients ΔT determined in the 15—60 °C range did not exceed 1.8 % °C^{-1}. The examined nitroalditols were stable in aqueous solution in this temperature range.

The data of Table 1 show no significant dependences of polarographic current on the structure and C-chain length of nitroalditols. This table lists the characteristic polarographic data as half-wave potentials ($E_{1/2}$ in phosphate pH 8 buffer) and their changes in relation to pH of the medium. The i_D change dependences of acidity are characterized by mean heights of polarographic waves at nominal pH values. Acetate buffer: pH 4 (96 mm), pH 4.6 (106 mm); phosphate buffer: pH 5 (112 mm), pH 6 (121 mm), pH 7 (116 mm); ammonium buffer: pH 9.4 (78 mm); carbonate buffer: pH 10.2 (33 mm).

Tracing of concentration dependences $i_D = f(c)$ of all nitroalditols under study was most important in the concentration range 5×10^{-5}—1×10^{-3} mol dm^{-3} in the phosphate pH 8 buffer at 20 °C. Calibration plots were processed by the linear regression method and parameters characterizing rather small series of experimental data (standard sample size $n = 10$ for evaluation S_r – relative standard deviations) were evaluated statistically (Table 2). Standard deviations of intercept (S_a) do not exceed ± 0.22 mm and

Table 1. Polarographic Data of Nitroalditols in Aqueous Solutions

1-Deoxy-1-nitro-alditol	$\dfrac{E_{1/2}}{V}$	$\dfrac{\Delta E_{1/2}}{V}$
-L-allitol	−0.95	0.37
-D-allitol	−0.94	0.36
-L-altritol	−0.93	0.29
-D-altritol	−0.94	0.28
-L-galactitol	−0.95	0.25
-D-galactitol	−0.95	0.34
-L-gulitol	−0.93	0.33
-D-gulitol	−0.92	0.31
-L-glucitol	−0.96	0.34
-D-glucitol	−0.96	0.34
-L-iditol	−0.94	0.31
-D-iditol	−0.94	0.34
-L-mannitol	−0.93	0.27
-D-mannitol	−0.95	0.25
-L-talitol	−0.92	0.30
-D-talitol	−0.92	0.32
-L-arabitol	−0.89	0.20
-L-*glycero*-L-*galacto*-heptitol	−0.99	0.33

$E_{1/2}$ – half-wave potential against saturated calomel electrode at pH 8 in phosphate buffer and c(nitroalditol) = 0.5 mmol dm^{-3}; $\Delta E_{1/2}$ – the shift of $E_{1/2}$ in the interval of pH 4.0—10.2.

Table 2. Evaluation of Calibration Graphs of Nitroalditols

1-Deoxy-1-nitro-alditol	$\dfrac{a}{mm}$	$\dfrac{b}{mm\ \mu mol^{-1}\ dm^3}$	r	$\dfrac{S_r}{\%}$
-L-allitol	0.80	0.411	0.9998	0.69
-D-allitol	0.49	0.359	0.9990	0.49
-L-altritol	0.73	0.381	0.9975	0.52
-D-altritol	0.79	0.308	0.9992	1.15
-L-galactitol	0.92	0.385	0.9982	0.59
-D-galactitol	0.64	0.355	0.9996	1.32
-L-gulitol	0.50	0.404	0.9998	1.19
-D-gulitol	0.37	0.393	0.9998	0.94
-L-glucitol	0.79	0.322	0.9975	1.31
-D-glucitol	0.77	0.321	0.9997	1.28
-L-iditol	0.45	0.415	0.9992	1.48
-D-iditol	0.83	0.386	0.9995	1.14
-L-mannitol	0.56	0.400	0.9991	0.30
-D-mannitol	0.72	0.402	0.9996	0.65
-L-talitol	0.80	0.318	0.9995	1.06
-D-talitol	0.61	0.358	0.9985	0.99
-L-arabitol	0.24	0.392	0.9993	0.59
-L-*glycero*-L-*galacto*-heptitol	0.54	0.401	0.9991	0.89

a – intercept, b – slope, S_r – relative standard deviation, r – correlation coefficient.

standard deviations of slope (S_b) ± 0.011 mm μmol^{-1} dm^3.

Polarographic data for H_2O_2 in the pH 4—10 interval: $E_{1/2} = -0.99$ V *vs.* SCE and the shift $E_{1/2} = 0.03$ V. The calibration plot for H_2O_2 in the concentration interval 5×10^{-5}—1×10^{-3} mol dm^{-3}

revealed following data: $a = (0.91 \pm 0.13)$ mm, $b = (0.213 \pm 0.03)$ mm μmol^{-1} dm^3, $r = 0.992$, $S_r = \pm 0.65$ %. Ammonium molybdate (0.003 mass %) did not display any wave at pH 8. Several decomposition catalysts of H_2O_2 were tried to suppress the H_2O_2 waves. As found, the H_2O_2 wave was totally suppressed by 10 mass % platinum on charcoal after 10 min.

Optimal values of the current—concentration relationships for nitroalditols measured in model oxidizing mixtures (5×10^{-4} mol dm^{-3} H_2O_2, 3 mg 10 mass % Pt—C, 0.003 mass % ammonium molybdate) were found to be $r = 0.997$ and higher and S_r not exceeding ± 1.48 %.

DISCUSSION

Linearity of the dependence of polarographic current on $h^{1/2}$ and low values of temperature coefficients corroborated the diffusion character of i_D of nitroalditols. The $E_{1/2}$ shift with increasing pH of the medium towards more negative values, as well as the simultaneous growth of waves towards their maximal height with a subsequent decrease indicate protonation of the nitro group [9]. The second more negative wave of nitroalditols ($E_{1/2}$ from -1.5 V to -1.65 V vs. SCE) shows only a half-magnitude corresponding to a two-electron process; it is insufficiently developed ($r < 0.9$) and therefore of no practical use for analytical purposes.

Evaluation of the more positive wave of nitroalditols (4e) affords correlation coefficient values evidencing a high probability level of linearity. The regression coefficient values are proportional to the sensitivity of the method, four-electron reduction and quality of atypical standards of nitroalditols. The values of slope are statistically significant from the coefficient of the regression lines. The low values of variation coefficients prove suitability of the direct polaro-graphic method for analytical determination. Application of optimal conditions found makes it possible to determine exactly nitroalditols even in oxidizing mixtures with the comparable amounts of H_2O_2 and catalytical amounts of Mo(VI). Statistical determination parameters decrease proportionally due to application of the Pt—C amount.

CONCLUSION

Optimal conditions for analytical determination of the functionally analytic group of nitroalditols suitable for monitoring their purity and stability in pure state, and oxidative decomposition mixtures with H_2O_2 and in the presence of Mo(VI) ions were elaborated. This method is also suitable for kinetic studies and controlling the nitromethane synthesis of saccharides.

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