Electroreduction of triose oximes

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Dedicated to Academician V Kellö, in honour of his 70th birthday

The reaction of DL-glyceraldehyde and 1,3-dihydroxy-2-propanone with hydroxylamine and the polarographic behaviour of oximes obtained were investigated in aqueous buffer solutions. As found, polarographic waves of these oximes in formate and acetate buffer solutions are pH-dependent within pH = 2—6. Both oximes were electroreduced on a preparative scale in the above-mentioned pH range of the reaction medium at potentiostatic and pH-static conditions. Mechanisms of the appropriate chemical and electrochemical reactions were proposed both from the polarographic and preparative electroreductions and reaction products.

Изучена реакция DL-глицеринового альдегида и 1,3-дигидрокси-2-пропанона с гидроксиламином, а также полярографическое поведение образовавшихся оксимов в водных буферных растворах. Обнаружены зависимости полярографических волн обоих оксимов от pH в интервале 2—6 в муравьинокислых и уксуснокислых буферных растворах. Проведено препаративное электровосстановление обоих оксимов в реакционных средах в упомянутом промежутке pH при потенциостатических и pH-статических условиях. Исходя из хода полярографического и препаративного электровосстановления и на основе образовавшихся продуктов было можно предложить механизмы соответствующих химических и электрохимических реакций.

As shown in our preceding paper on electroreduction of the oximes of glycolaldehyde and of its *O*-methyl derivative, not only the oxime group could undergo reduction, but also an electroreductive cleavage of the hydroxyl or *O*-methyl group can take place to yield the unexpected ethylamine [1]. These results stimulated us to examine the electroreduction of triose oximes aiming to throw more light on the unusual course of their behaviour.

Experimental

The polarographic waves were recorded on an LP 7 polarograph (Laboratorní přístroje, Prague) using a usual polarographic Kalousek vessel with a separated saturated

calomel electrode (SCE). Compounds were electroreduced on a preparative scale in an electrolyzer under potentiostatic and pH-static conditions, as described in our preceding paper [2] and patented procedure [3]. The required potential of the working mercury electrode with respect to SCE was controlled by the potentiostat PRT 40-5X (Tacussel, France). The adjusted pH value was controlled by a TTT2 Titrator (Radiometer, Copenhagen). The products were identified by ^{13}C NMR spectra taken with an FT spectrometer AM-300 (Bruker, GFR) operating at 75.432 MHz and 25 °C.

DL-Glyceraldehyde, 1,3-dihydroxy-2-propanone, propenal, 1-aminopropane, 2-aminopropane, 3-amino-1-propene, 3-amino-1-propanol, and 3-amino-1,2-propanediol were Fluka (Switzerland) chemicals, hydroxylammonium sulfate was a commercial product of Lachema, Brno. Other chemicals for buffers, polarography, chromatography, and electrolysis on preparative scale were of anal. grade.

Isolation and identification of products

Solutions of DL-glyceraldehyde and 1,3-dihydroxy-2-propanone oximes for polarography and preparative electroreduction were prepared in the same way as described for oximes of glycolaldehyde and of its *O*-methyl ether [1]. Like were also monitoring of the electroreduction and analyses of amines obtained by paper chromatography and ^{13}C NMR spectroscopy.

Solutions after preparative electroreduction of triose oximes lasting 3—5 h were treated with barium formate; barium sulfate was filtered off, the solution of amine formates concentrated under reduced pressure to a small volume was transferred into a cellulose-packed column (100 cm × 5 cm) and separated using the solvent system butanol—formic acid—water (φ_r = 8 1 1) at a 15 $cm^3 h^{-1}$ flow rate. Separation was monitored by paper chromatography on Whatman 3M paper in the same solvent system, the spots being visualized by spraying with 0.1 % butanolic solution of ninhydrine and heating to 105 °C. The individual amines were identified by ^{13}C NMR spectroscopy and the structure was verified by comparison with the specimens, or, where these were not at disposal, the multiplicity of signals was estimated from ^{13}C NMR spectra without decoupling, or by the INEPT method.

The preparative electroreduction of oximes of both trioses was studied in the pH = 2.8—6.0 range; the single products were isolated from experiments carried out at pH = 3.6 and 6.0 by column chromatography on cellulose. Preparative electroreduction of DL-glyceraldehyde oxime (100 cm^3, 0.1 M) in the presence of a 50 % excess of hydroxylammonium sulfate in formate buffer solution of pH = 3.6 and at the potential of working mercury electrode −1.4 V afforded four substances in the crude product, as evidenced by paper chromatography and ^{13}C NMR spectra showing four spots and twelve signals, respectively. The products were separated by column chromatography on cellulose and identified as formates of 3-amino-1,2-propanediol (1054 mg, 77.5 %), 3-amino-1-propanol (160 mg, 13.3 %) and a mixture of 3-amino-1-propene and 1-aminopropane (90 mg, 8.6 %). Mobility of the salts on paper or the cellulose column rose in the series 3-amino-1,2-propanediol, 3-aminopropanol, 3-amino-1-propene, 1-aminopropane. Signal positions in the spectra recorded in D_2O against methanol as an internal reference

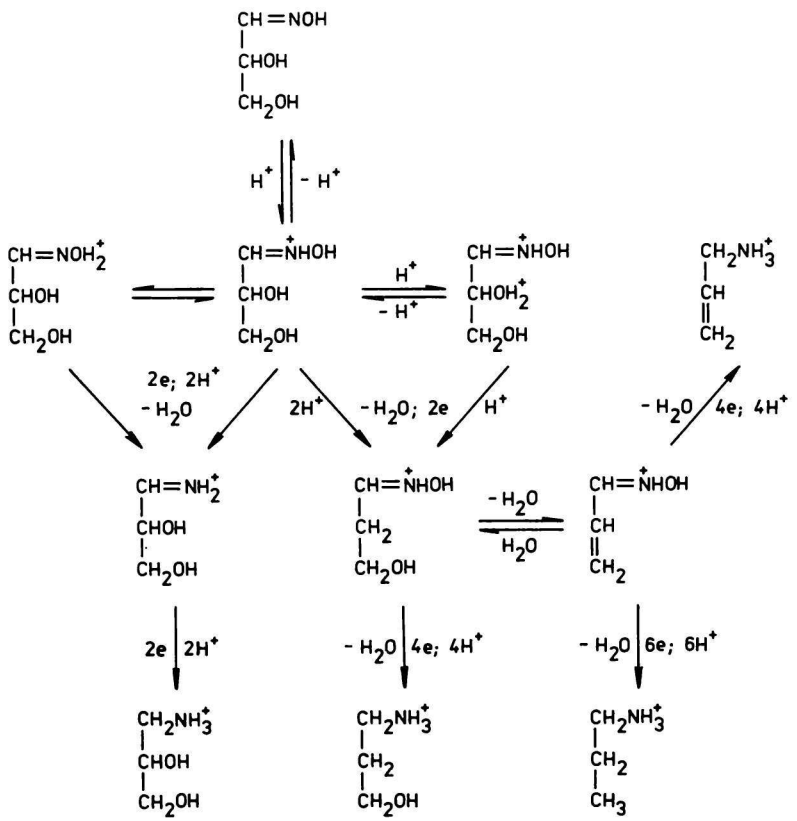
($\delta(CH_3OH)$: δ(tetramethylsilane) = 50.15 ppm) for 3-amino-1,2-propanediol at δ/ppm: 43.0, 64.5, 69.1, for 3-aminopropanol at 30.2, 38.5, 60.1, for 3-amino-1-propene at 42.6, 121.8, 130.5, and for 1-aminopropane at 11.3, 21.4, 42.8 were consistent with those of the respective specimens. Decrease of pH values of the reaction medium was associated with a decrease of the fundamental amine, *i.e.* 3-amino-1,2-propanediol, whilst the amount of the remaining three amines increased proportionally as shown by chromatographic and ^{13}C NMR spectral analyses. On the other hand, an increase of pH values of the reaction medium favourized the increase of the fundamental amine over other amines. Thus, a preparative electroreduction of DL-glyceraldehyde oxime (100 cm^3, 0.1 M) in the presence of a 100 % excess of hydroxylammonium sulfate at pH = 6.0 and at the potential of working mercury electrode −1.5 V afforded virtually the expected 3-amino-1,2-propanediol (1210 mg, 96.0 %) and a small amount of 3-aminopropanol (12 mg, 2 %). 3-Amino-1-propene and 1-aminopropane originated in trace amounts only as evidenced by paper chromatography. Also propenal oxime was electroreduced as a model substance at pH = 3.6 under the same conditions as with DL-glyceraldehyde oxime to elucidate formation of the unexpected 3-amino-1-propene and 1-aminopropane; origination of both amines as main products of electroreduction was proved by chromatographic and ^{13}C NMR spectroscopic methods. Also a spot of 3-aminopropanol appeared on the chromatogram.

Electroreduction of 1,3-dihydroxy-2-propanone oxime in the pH = 2.8—6.0 range yielded three amines. At pH = 3.6 and −1.4 V of the working mercury electrode potential, 100 cm^3 of the 0.1 M solution with a 50 % excess of hydroxylammonium sulfate in formate buffer solution furnished a mixture, which on separation on a cellulose-packed column afforded formates of 2-aminopropane (930.7 mg, 89.5 %), 2-amino-1-propanol (72 mg, 6 %) and 2-amino-1,3-propanediol (41.0 mg, 3.0 %). At a lower pH than 3.6 virtually the sole 2-aminopropane was obtained. On the other hand, at pH values higher than 3.6 yields of 2-aminopropane decreased in favour of the remaining two amines. Electroreduction of 1,3-dihydroxy-2-propanone (100 cm^3, 0.1 M) in the presence of hydroxylammonium sulfate in a 100 % excess at pH = 6 and −1.5 V of the working mercury electrode potential and work-up gave 2-aminopropane (160 mg, 15.4 %), 2-amino-1-propanol (159 mg, 13.3 %), and 2-amino-1,3-propanediol (856 mg, 63.0 %) as formates. The ^{13}C NMR spectrum of these three amines consisted of only seven signals, since 2-aminopropane and 2-amino-1,3-propanediol exhibit molecular symmetry. Specimen of the former disclosed an identical spectrum (δ = 21.1, 45.4 ppm). Identification of the other two amine formates was based on the multiplicity of the respective signals in the ^{13}C NMR spectrum without decoupling as follows: 2-amino-1-propanol, δ/ppm: 15.4 (C-3—CH_3), 50.4 (C-2—CH), 63.8 (C-1—CH_2); 2-amino-1,3-propanediol, δ/ppm: 55.5 (C-2—CH), 60.0 (C-1—CH_2 and C-3—CH_2).

Results and discussion

DL-Glyceraldehyde and 1,3-dihydroxy-2-propanone oximes undergo electroreductions in acid media, which was seen as two polarographic waves; their heights and mutual ratios depended on pH values of the medium in the same

way as evidenced with the oximes of glycolaldehyde and of its *O*-methyl derivative [1]. Polarographic study of reduction of both triose oximes showed the optimal region for their preparative electroreduction to be in the pH = 2.6—6.0 range. In more acid media a decomposition of the oximes under study took place and at pH ≈ 6.0 the amount of the reduced forms considerably decreased. At least a 50 % excess of hydroxylammonium sulfate was needed to prevent regeneration of trioses from their oximes in the course of electroreductions.



Scheme 1

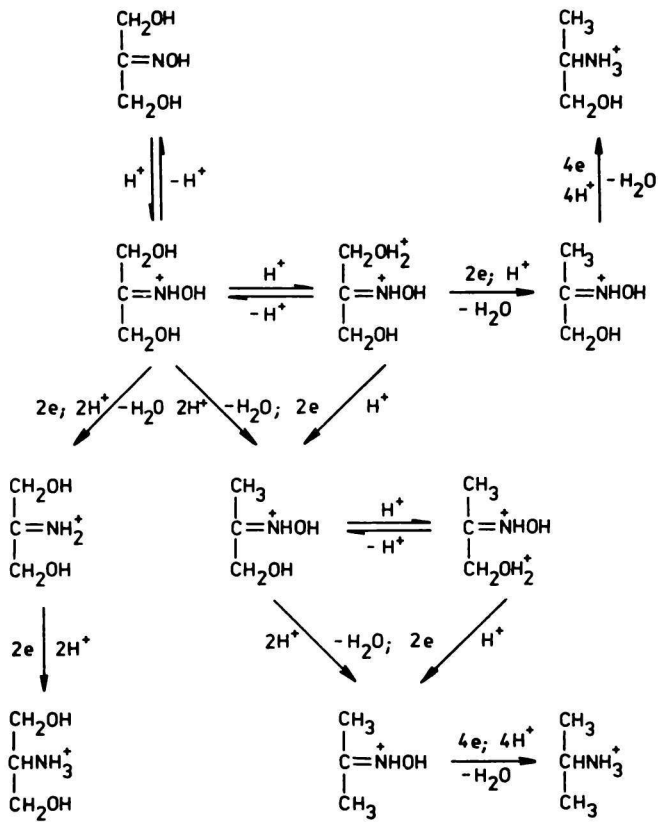
As found, oximes of both trioses can undergo, in addition to electroreduction of the oxime group, even a hydrogenolysis of the adjacent hydroxyl groups: 1,3-dihydroxy-2-propanone afforded three possible amines — 2-amino-1,3--propanediol, 2-amino-1-propanol, and 2-aminopropane. DL-Glyceraldoxime can produce on electroreduction even four products (3-amino-1,2-propanediol,

3-amino-1-propanol, 3-amino-1-propene, and 1-aminopropane) and therefore, not only an electroreductive cleavage of a hydroxyl group in α-position, but also a chemical elimination of the hydroxyl group in β-position occurred under formation of other oximes. The variability of amino products obtained by electroreduction of oximes of both trioses depending on changes in the pH values of the medium can be rationalized by a possible protonation even of hydroxyl groups during electroreduction. Results of the polarographic study and the character of products obtained by electroreduction of DL-glyceraldoxime in relation to pH of the medium allow to propose the mechanism of the appropriate chemical and electrochemical reactions (Scheme 1).

The finding that oximes under investigation undergo electroreduction exclusively in acid media provides an evidence for electroactivity of the protonated forms only. The fundamental presupposition for electroreduction of these compounds is the protonation of their oxime groupings [1, 4]. Thus, the main process to electroreduce the DL-glyceraldoxime at pH = 6, is the four-electron reduction of the protonated form of its oxime group under formation of 3-amino-1,2-propanediol. Moreover, a small amount of 3-aminopropanol was formed under this condition, which means that the secondary alcoholic group in the reduced compound could be cleaved during the electroreduction. This is an analogous process to that described with the electroreduction of DL-glyceraldehyde itself [5]. The change in the mutual ratio of products originating by electroreduction of DL-glyceraldoxime with the pH indicated a possible protonation even of its hydroxyl groups, which, in turn made the electroreductive cleavage easier under formation of further two oximes able to enter the reaction, *i.e.* oximes of 3-hydroxypropanal and propenal. The main portion of 3-hydroxypropanal oxime evidently originated by reduction of DL-glyceraldoxime protonated not only at the oxime, but also at the adjacent hydroxyl group. The intermediate formed from such an oxime by electroreductive cleavage of the hydroxyl ion was either neutralized to 3-hydroxypropanal oxime or eliminated the primary alcoholic group to yield propenal oxime. It is noteworthy that electroreduction of both these oximes can lead similarly to the following products — 3-aminopropanol, 3-amino-1-propene, and 1-aminopropane. Origination even of 3-aminopropanol on electroreduction of the model propenal oxime evidenced that the latter formed an equilibrium with 3-hydroxypropanal oxime, this being analogous to that of propenal alone with 2-hydroxypropanal [6]. The main products of electroreduction of propenal oxime were found to be 3-amino-1-propene and 1-aminopropane. It is supposed that formation of the latter followed the mechanism valid for reduction of propenal itself [7]. It is evident that protonation reactions shown in Scheme 1 took place in the neighbourhood of the mercury electrode at the polarized oxime molecules only, since electroreductions were carried out at pH > 2, *i. e.* at a substantially higher

values than are the pK_a values of conjugated acids of oximes and aliphatic alcohols [8, 9].

Knowledge on the electroreduction of 1,3-dihydroxy-2-propanone oxime entitled us to propose a similar mechanism (Scheme 2) with some deviations due to differences in structures of oximes of both trioses. Even in this case only the protonated form of oxime underwent electroreduction. The main product of electroreduction of 1,3-dihydroxy-2-propanone oxime at pH = 6 was 2-amino--1,3-propanediol accompanied by 2-amino-1-propanol and 2-aminopropane. Formation of the last two compounds indicated the possibility to cleave one or both nonprotonated hydroxyl groups in the neighbourhood of the protonated oxime group during electroreduction. Increase of acidity of the medium was associated with the increase of 2-aminopropane formation, thus proving an enhancement of participation of protonated hydroxyl groups in electroreduction of the particular oxime.



Scheme 2

Although electroreductive cleavage of hydroxyl groups has to precede the reaction with respect to electroreduction of the oxime grouping, still it was impossible to obtain such oximes. Protonated forms of oxime group prompted cleavage of the adjacent hydroxyl group of oximes of both trioses by their polarization effect similarly, as with trioses alone [2, 5]. Here, products with preserved carbonyl groups can be obtained, because their electroreduction proceeded at more negative potentials than with the protonated azomethine grouping.

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