Reactions of Saccharides Catalyzed by Molybdate Ions XLV.* Utilization of Molybdic and Peroxomolybdic Acids for Preparation of Aldoses

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Dedicated to Dr. Ing. Š. Bauer, DrSc., in honour of his 70th birthday

Molybdic acid epimerizes aldoses under formation of an equilibrium mixture consisting of C-2 epimeric aldoses, whereas peroxomolybdic acid inhibits the epimerization reaction. Peroxomolybdic acid was also responsible for both the stereoselective hydroxylation of glycals to aldoses with a *cis* arrangement of hydroxyl groups at carbon atoms C-2 and C-3 and oxidative decomposition of alkali metal salts of 1-deoxy-1-nitroalditols to the corresponding aldoses; it simultaneously prevented the subsequent epimerization of aldoses being formed.

Molybdate complexes of many monosaccharides in aqueous solutions of acids were evidenced by various methods (polarimetry, electrophoresis, potentiometric titration, circular dichroism, NMR spectroscopy, and biologic procedures). Molybdic acid, similarly as tungstic acid afforded the corresponding peroxo acids in the presence of hydrogen peroxide. Peroxomolybdic acid was first used in the chemistry of saccharides for oxidation of aldose diethyl thioacetals to the corresponding diethyl sulfones [1]. In our research project molybdic acid was employed as a catalyst in the mutual transformation of C-2 epimeric aldoses. Peroxomolybdic acid was used for hydroxylation of glycals to aldoses and also for degrading 1-deoxy-1-nitroalditols to the corresponding aldoses. This paper concerns examination of the influence and behaviour of these acids in the above-mentioned reactions.

Molybdate ions form complexes with aldoses, which are responsible for their epimerization. This reaction of general use was verified also on aldotetroses up to aldooctoses [2]. The optimal pH for epimerization of aldoses varied within 1.5 and 3 [3] and the reaction rate depended on the conditions; it is worth noting that composition of the equilibrium mixture of C-2 epimeric aldoses remained constant in the temperature range 28—90 °C [4]. Recently, we found with selected aldopentoses up to aldooctoses and gentiobiose that epimerization did not proceed in the presence of peroxomolybdic acid. D-Glucose and D-mannose underwent a partial oxidation to the corresponding aldonic acids at an extended reaction time (from 3 h to 12 h); these acids were concurrently degraded to yield a small amount of D-arabinose (2—5 %). D-Arabinose originating in this way was also partially oxidized to arabonic acid (the over-all yield of gluconic and arabonic, or alternatively mannonic and arabonic acids was 40 % with regard to the starting aldohexose).

Aqueous solutions of glycals were converted stereospecifically with peroxomolybdic acid to aldoses with a *cis* arrangement of hydroxyl groups at carbon atoms C-2 and C-3 [5—7]. The pH optimum for a stereoselective hydroxylation of glycals is within 4 and 5 [6]. Aqueous solutions of glycals entered complexes with molybdate ions as evidenced *e.g.* by the change of their specific rotation in relation to the pH value; D-galactal revealed the greatest changes in specific rotation in the pH range 4—5 (Table 1). The highest specific rotation values of a series of selected aldoses in molybdate solutions were found to be at pH 5.6, lower ones at pH 4.6. Similarly, the change in specific rotation in the presence of peroxomolybdic acid occurred at pH 4.6 (Table 2). These results let us conclude that molybdic and peroxomolybdic acids deposited complexes with

Table 1. Dependence of Specific Rotation of D-Galactal in Aqueous Molybdate Solutions on pH of the Solution

$[\alpha]$(D, 21 °C)/°	pH
+ 2	2.2
+ 17	3.2
+ 30	4.1
+ 18	4.8
+ 6	5.6
+ 4	6.0
− 1	8.3

$[\alpha]$(D, 21 °C, water) = − 5°

* For Part *XLIV* see *Chem. Papers 45*, 829 (1991).

Table 2. Specific Rotations [α]/° of Aldoses in Various Conditions

Aldose	H_2O	Mo^{VI} pH 5.6	Mo^{VI} pH 4.6	Mo^{VI}, H_2O_2 pH 4.6
D-Lyxose	– 14.0	– 57	– 29	– 23
D-Ribose	– 20.5	– 81.5	– 38	– 37
D-Mannose	+ 14.6	– 33.5	– 17	– 13
D-Talose	+ 20.8	+ 63.5	+ 32	+ 12

aldoses. Conversion of monosaccharide glycals, maltal, and lactal with peroxomolybdic acid varied within 75 and 90 % with regard to aldoses with a *cis* arrangement of hydroxyl groups at carbon atoms C-2 and C-3; conversion to the complemental epimeric aldose was 2—5 %. It has been assumed that the high stereoselectivity of hydroxylation was due to origination of a complex between peroxomolybdic acid and the hydroxyl group of a glycal at C-3; this consideration was now backed by the finding that on substitution of this group, as *e.g.* with 3-*O*-methyl-D-glycal, 3-*O*-methyl-D-glucose and 3-*O*-methyl-D-mannose were obtained in a 1 1 ratio [6]. The effect of substitution of a hydroxyl at C-4 was not substantial as demonstrated with hydroxylation of maltal and lactal giving epimaltose (83 %) and epilactose (73 %), respectively, in high yields [7]. Peroxomolybdic acid fully inhibited the epimerization reaction and therefore, the ratio of epimeric aldoses formed during the hydroxylation process was constant.

As found, peroxomolybdic acid converted 1-deoxy-1-nitroalditols in alkaline aqueous solutions to the corresponding aldoses [8]. An oxidative degradation of 1-deoxy-1-nitro-L-mannitol yielded 71 % of L-mannose. The general validity of this reaction was demonstrated successfully with extension of carbon chains of several aldopentoses, aldohexoses, and aldoheptoses. The originally strong alkaline medium (pH 11) turned rapidly to pH 5—6 as a consequence of an oxidative decomposition of nitroalditol salts. Similarly as with hydroxylations of glycals, peroxomolybdic acid fully inhibited epimerization of aldoses formed during the oxidative degradation of 1-deoxy-1-nitroalditols.

Molybdic acid was used for epimerizations of aldoses in catalytical amounts and so was also peroxomolybdic acid for hydroxylation of glycals and oxidative decomposition of alkali metal salts of nitroalditols, but hydrogen peroxide was present in a great excess.

EXPERIMENTAL

Specific rotation of saccharides under examination was measured with an automatic polarimeter type 241 (Perkin—Elmer), pH of solutions was determined with a Standard PHM-82 (Radiometer, Copenhagen) apparatus. Conversion of aldoses was monitored by paper chromatography on a Whatman No. 1 paper in the 1-butanol—ethanol—water system (φ_r = 5 : 1 : 4) at the elution time 20—30 h, detection was carried out with anilinium hydrogen phthalate or by the Trevelyan method [9]. The saccharides were separated on a preparative scale on a Dowex 50W, X-8 column (120 x 3 cm) with particles size 0.07—0.15 mm in Ba^{2+} form, elution with water at a 13 cm^3 h^{-1} flow rate.

Specific Rotation of D-Galactal in Molybdate Solutions

Specific rotation of D-galactal (ρ = 1 g dm^{-3}) in aqueous solution of ammonium molybdate (ρ = 4 g dm^{-3}) was measured at pH 5.6. Various pH of solutions was adjusted by adding hydrochloric (pH = 2.2) or acetic (pH = 3.2—4.8) acids, or sodium hydroxide (pH = 6.0 and 8.3) (Table 1).

Specific Rotation of Aldoses in Molybdate Solutions in the Presence of Hydrogen Peroxide

Specific rotation of aldoses (ρ = 1 g dm^{-3}) was measured in the respective aqueous solution, aqueous ammonium molybdate (ρ = 4 g dm^{-3}) of pH 5.6 and pH 4.6 (adjusted with acetic acid), or in hydrogen peroxide solution (ρ = 5 g dm^{-3}) of pH 4.6.

Epimerization of Aldoses in the Presence of Molybdate Ions and Hydrogen Peroxide

Aldose (D-ribose, D-arabinose, D-xylose, D-glucose, D-mannose, D-galactose, D-talose, D-*glycero*-D-*galacto*-heptose, D-*erythro*-L-*gluco*-octose) (50 mmol) or gentiobiose (1 mmol), ammonium molybdate (25 μmol), hydrogen peroxide (15 mmol), and water (2.5 cm^3) were heated at 90 °C for 3 h. Paper chromatography did not show the presence of the corresponding C-2 epimeric saccharides.

Oxidation of D-Glucose and D-Mannose with Peroxomolybdic Acid

D-Glucose monohydrate (19.8 g; 0.1 mol), ammonium molybdate (0.62 g; 0.5 mmol), hydrogen

peroxide (30 cm^3, 30 %, 0.3 mol), and water (60 cm^3) were heated at 90 °C for 12 h. Paper chromatography of the mixture disclosed the presence of D-glucose, D-arabinose, and aldonic acids. The mixture was cooled, palladium on charcoal (0.1 g) was added and the content was allowed to stand for 1—2 d. The mixture was diluted with water to 400 cm^3, the pH was adjusted with 0.1 M-NaOH to 6.5 and baker's yeast (3 g) was added. The mixture was filtered after D-glucose had been consumed (5 to 6 d), purified by addition of charcoal, deionized with cation and anion exchangers (25 cm^3 of Ostion KS 0210 in H^+ form and 300 cm^3 of Wofatit SBW in HCO_3^- form) and the filtrate was concentrated into a sirupy consistence. It was fractionated on a Dowex 50W (Ba^{2+} form) column with water: the first fraction (765—1100 cm^3) contained D-arabinose (0.4 g, 3 %), but no D-ribose. The anion exchanger afforded on deionization with formic acid (10 vol. %) a mixture (6.2 g, 38 %) of gluconic and arabonic acids.

The same procedure applied for D-mannose (18 g) yielded D-arabinose (0.5 g, 4 %), a mixture of mannonic and arabonic acids (6.8 g, 41 %), but no D-ribose.

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