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Comparative study of homogeneous hydrogenation of D-glucose and D-mannose catalyzed by water soluble [Ru(tri(*m*-sulfophenyl)phosphine)] complex

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Abstract

Homogeneous hydrogenation of two epimeric aldoses, D-glucose (D-Glc) and D-mannose (D-Man) was performed in water, with molecular hydrogen and by transfer hydrogenation catalyzed by [Ru–TPPTS] complex (TPPTS = trisodium salt of tri(*m*-sulfophenyl)phosphine). Both method proved effective, and revealed D-Man as more reactive aldose. Hydrogen transfer has been studied with various hydrogen donors; the most effective, but highly pH-dependent system has been found in Et_3N/formic acid (azeotropic mixture 2:5) as the source of hydrogen.

Keywords: (Sulfophenyl)phosphine derivatives; Phosphine derivatives; Ruthenium; Formiates; Sodium; Ammonium; Hydrogenation

1. Introduction

The origins of our venture into the realization of a 'comby' process, i.e. contemporaneous catalytic epimerization–hydrogenation of aldoses, are outlined in the previous paper [1]. We now present the results of our study of the relative rates of homogeneous hydrogenation of D-glucose (D-Glc) and D-mannose (D-Man) catalyzed by water soluble [Ru–TPPTS] complex (TPPTS = trisodium salt of tri(*m*-sulfophenyl)phosphine). This ligand was introduced by Kuntz [2,3]; its electronic properties and various catalytic effects of its complexes are reported [4,5]. We paid particular attention to the effects of hydrogen source, the pH, and the added salt on the relative rates of hydrogenation of two aldoses. Hydrogenation of aldoses in water catalyzed by homogeneous catalyst under hydrogen, or in the presence of another hydrogen source, has not been studied as yet.

2. Experimental

2.1. General

^{1}H- and ^{13}C-NMR spectra were obtained on JEOL FX 900FT and Varian XL-GEM 300 spectrophotometer; shifts are given in ppm downfield from TMS. GLC analyses were performed on Hewlett Packard GC 5890 chromatograph with flame ionization detector (FID), HP 3396A integrator and capillary HP-17 column.

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HPLC analyses were performed on Hewlett Packard instrument with 1050 pump, HP 1047A refractometric detector and HP 3396A integrator, on Aminex HPX 87C column (Bio-Rad), thermostated at 85°C in automatically controlled thermostat.

2.2. Materials

D-Glc, D-Man (p.a., Fluka) were dried in vacuo for 24 hours before use. Formic acid, triethylamine, $RuCl_3 \cdot 3H_2O$ (p.a., Kemika), NaI (p.a., Medica), hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS) (p.a., Fluka) were used as received. Redistilled water and p.a. organic solvents stored under nitrogen, were used in all experiments.

$RuCl_2(PPh_3)_3$ was prepared by a published method [6].

TPPTS was obtained from Hoechst AG (Frankfurt) as ca. 33% aqueous solution.

2.2.1. Preparation of [Ru–TPPTS] complex (according to Basset [7]).

TPPTS (2.4 ml of 33% aq. solution) was diluted with 10 ml of water and added dropwise, under vigorous stirring, to the solution of $RuCl_2(PPh_3)_3$ (0.54 g, 0.56 mmol) in THF (60 ml), preheated at 60°C. The reaction mixture was stirred and heated under reflux for 30 min, then organic phase was decanted, and aqueous layer evaporated to dryness. It was obtained 1.05 g of the product which was used as catalyst without ulterior purification. ^{13}C-NMR ($CDCl_3$): 12.55, 130.64 (J(P–C) 6 Hz), 131.26 (J(P–C) 24 Hz), 137.29 (J(P–C) 16 Hz), 137.49 (J(P–C) 14 Hz), 144.09 (J(P–C) 7 Hz).

2.2.2. Hydrogenation under hydrogen pressure

Hydrogenation under hydrogen pressure was performed in Parr M 4561 autoclave, volume 300 ml, connected to a cooling water and temperature controller Parr series 4841. Samples were taken trough a sampling tube at regular time intervals, and controlled by HPLC.

In the standard experiment aldose (3.6 g, 20 mmol), [Ru–TPPTS] (0.30 g, 0.1 mmol), and sodium iodide (1.5 g, 10 mmol) were dissolved in 100 ml of water, and reaction started by applying hydrogen under pressure.

2.2.3. Hydrogenation under hydrogen transfer

Hydrogenation under hydrogen transfer was performed in a double-walled reactor, volume 50 ml, thermostated by Haake L circulator thermostat with silicon oil as the heating medium. The aldose (0.36 g, 2 mmol) and sodium formiate (0.7 g, 10 mmol), or ammonium formiate (0.63 g, 10 mmol) or azeotropic mixture of Et_3N/formic acid (10 mmol) were dissolved in water (10 ml) and preheated at 100°C. Reaction was started by addition of [Ru–TPPTS] complex (0.05 g, 0.02 mmol). During reaction pH was controlled by thermostable combined pH electrode 'pH C2401' (Radiometer), and was kept constant by addition of dill. formic acid. Samples (0.03 ml) were taken by siring at regular time intervals, evaporated and dried in vacuum desiccator at 50°C, dissolved in 0.05 ml of pyridine and silylated by adding of HMDS (0.05 ml, 6 mol) and TMCS (0.025 ml, 2.3 mmol). The progress of the hydrogenation was monitored by GLC with temperature program from 150 to 170°C at 2°C/min.

3. Results and discussion

3.1. Homogeneous catalytic hydrogenation with molecular hydrogen

Traditionally, sugars are hydrogenated to the corresponding alditols by heterogeneous catalysts at elevated temperatures and hydrogen pressure [8]. Homogeneous catalytic hydrogenation of aldehyde carbonyl group in general, and of aldoses in particular, was scarcely reported in the literature [9,10]. We therefore started this study by searching the conditions where hydrogenation of the two epimeric aldoses can be completed with different reaction rates, with D-Man as more reactive counterpart. Positive

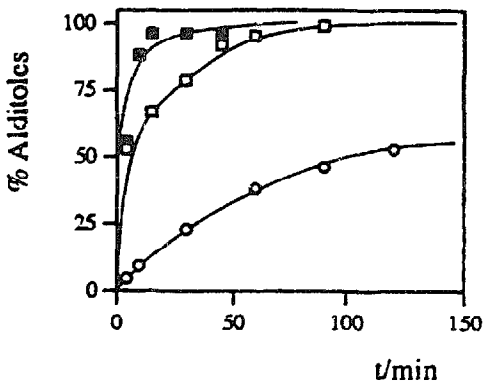

Fig. 1. Progress curve for the hydrogenation of D-Glc and D-Man catalyzed by [Ru–TPPTS] complex in water at 100°C and 50 atm; ◪ D-mannitol, □ D-sorbitol, and hydrogenation of D-Man in the absence of NaI: ○ D-mannitol.

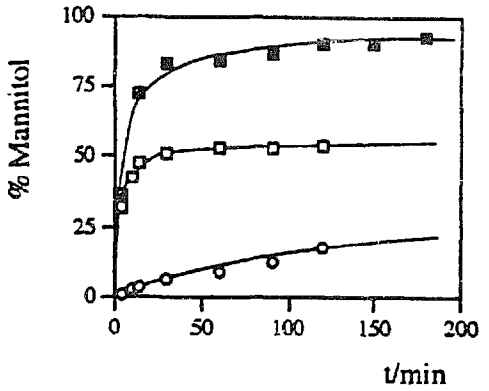

Fig. 2. Progress curve for the transfer hydrogenation of D-Man catalyzed by [Ru–TPPTS] complex in water at 100°C with ◪ NEt_3/formic acid (2:5), □ Na formate, ○ NH_4 formate.

outcome of this study prospects selective hydrogenation of D-Man, as formed from D-Glc in the epimerization process. In the first series of experiments we carried out the reduction of D-Glc and D-Man with [Ru–TPPTS] complex according to Basset et al. [7]; in water at 100°C, at hydrogen pressure of 50 atm, in the presence and absence of NaI, Fig. 1.

Faster hydrogenation of D-Man was observed, as expected, since the difference in the ground state energies of D-Glc and D-Man renders the latter more reactive. Thus, after 15 min D-Man was nearly completely hydrogenated, while only 65% of D-Glc was converted in the same reaction time. In the absence of NaI conversion of D-Man was ca. 6 times slower, however. The promoting effect of this salt on hydrogenation of aldoses probably takes place according to the same mechanism proposed by Basset [11] for propionaldehyde. Sodium ion effects carbonyl group by changing coordination from an η-2 to a η-1 mode, preventing hydride transfer to the carbon atom of aldehyde and affording an alkoxide ion which is coordinated by carbon atom to the metal center [9].

3.2. Homogeneous catalytic transfer hydrogenation

Transfer hydrogenation of D-Man with complex [Ru–TPPTS] was carried out in water at 100°C. As the hydrogen donor sodium formiate, ammonium formiate, or azeotropic mixture of formic acid and triethylamine (Et_3N/formic acid 5:2) were used. This latter reagent was successfully used by Brunner and Leitner in catalytic transfer hydrogenation of α,β-unsaturated carboxylic acids [12–14].

Conversion was monitored by GLC and the results in Fig. 2 revealed that this process strongly depends on the formiate counterion. Thus, after 180 min D-Man was nearly completely hydrogenated in the mixture of Et_3N/formic acid (2:5), while with sodium formiate and ammonium formiate conversion was much lower. Contrary to the effect of NaI in hydrogenation with molecular hydrogen, when the same reaction was carried out with

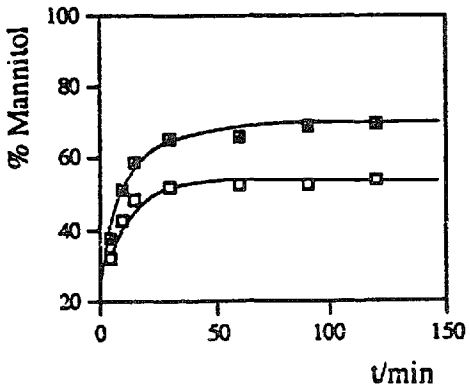

Fig. 3. Progress curve for the transfer hydrogenation of D-Man catalyzed by [Ru–TPPTS] complex in water at 100°C with Na formate: □ with NaI, ◪ without NaI.

Table 1
Transfer hydrogenation of aldoses catalyzed by water soluble [Ru–TPPTS] complex with mixture of NEt_3/formic acid (2:5) at 100°C

Substrate	Conversion after 3 h (%)	Selectivity (%)	Yield of alditol (%)
D-glucose	80	64	51
D-mannose	93	93	86

sodium formiate as hydrogen donor in the presence of NaI, lower yields were obtained than in the absence of the salt, Fig. 3.

Having been confirmed as the best source of hydrogen Et_3N/formic acid (2:5) was investigated in comparative hydrogenation of D-Glc and D-Man; higher reactivity of D-Man was again observed, Table 1 and Fig. 4.

Importantly, during hydrogenation of aldoses [Ru–TPPTS] complex was not deactivated by carbonylation as repeatedly observed in organic solvents for Ru and Rh complexes with lipohilic phosphine ligands [15–18].

In the last series of experiments we have studied the pH dependence of the transfer hydrogenation of D-Man and Et_3N/formic acid (2:5) as hydrogen source. Fig. 5. This correlation is important in view of coupling this process with C(2) epimerization catalyzed by heptamolybdate ion. It is known that in the acidic medium the rate of epimerization decreases ca. 20 times by raising the pH from 2.5 to 5.9 [19].

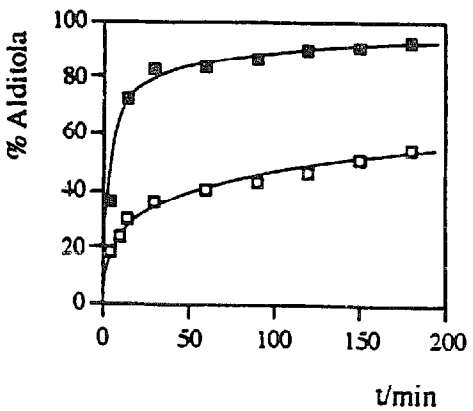

Fig. 4. Progress curve for transfer hydrogenation of D-Man i D-Glc catalyzed by [Ru–TPPTS] complex with NEt_3/formic acid (2:5) in water at 100°C; □ D-sorbitol, ◪ D-mannitol.

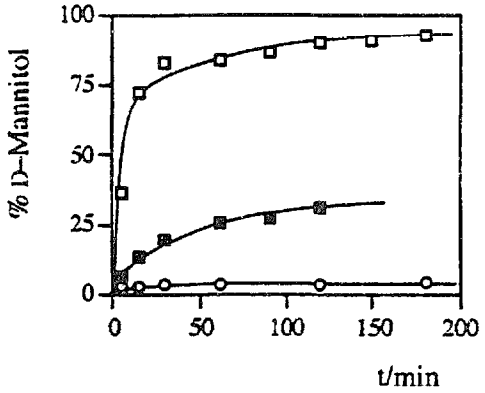

Fig. 5. Progress curve for the transfer hydrogenation of D-Man catalyzed by [Ru–TPPTS] complex with NEt_3/formic acid (2:5) in water at 100°C: □ pH = 8.0–8.4, ◪ pH = 6.5–7.0, ○ pH = 5.0–5.5.

This transfer hydrogenation turned out to be strongly pH dependent, however, see Fig. 5. The highest rate was observed at pH 8.0–8.4; strongly diminished catalytic efficiency was observed already at pH 5.0–5.5, i.e. at the upper pH limit for C(2) epimerization.

In conclusion, water soluble ruthenium complex with sulfonated phosphine ligand (TPPTS) is an effective and selective catalyst for hydrogenation of aldoses either under hydrogen pressure or by hydrogen transfer. However, it could not be used in a 'comby' process with heptamolybdate ion because the optimal pH range for its activity significantly differs from that where heptamolybdate ion is effective in C(2) epimerization. Continuing this project we therefore envisage combining chemical catalyst for C(2) epimerization with the biocatalytic reduction step.

Acknowledgements

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