

Comparative study of C(2) epimerization of D-glucose and D-mannose catalyzed by water soluble organometallic complexes with nitrogen ligands

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Abstract

Epimerization of D-glucose and D-mannose, catalyzed by the water soluble complexes of Cu(II), Ni(II), Co(II) and Cd(II) with bisnitrogen ligands 4–7, and by Mo(VI) complexes prepared in situ from ammonium heptamolybdate (AHM) with ligands 4–9 is compared. All examined complexes exhibit lower catalytic activity than AHM; strong coordination of the ligands by both (N,O) heteroatoms to metal ions, presumably affords catalytically less active species. Some free ligands and their metal (II) complexes catalyze both C(2) epimerization and isomerization of aldoses to D-fructose.

Keywords: Ethylenamines; Copper; Nickel; Cobalt; Cadmium; Epimerization; Isomerization

1. Introduction

Continuing our study of the ammonium heptamolybdate (AHM) catalyzed C(2) epimerization of aldohexoses [1–3], and aldopentoses [4], we recently reported [5] the kinetic and thermodynamic data of C(2) epimerization of D-mannose (D-Man) to D-glucose (D-Glc) in acetonitrile–water. Small shifts of the equilibrium $D-Glc \rightleftharpoons D-Man$ in favour of D-Man were observed in the mixtures of these two solvents. Commercial interest in the catalytic C(2) epimerization of aldoses resides in the opportunity to obtain valuable C(2) epimers from their

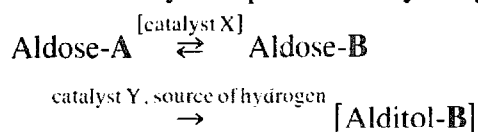
more widespread counterparts in nature, and after subsequent high-pressure hydrogenation and separation of two polyols, to yield the less available C(2) epimeric polyol. This process is presently performed in two separate steps; in the first one isomerization of the more available aldose, e.g. D-Glc or D-Xyl, is completed and in the second one, after separation of the AHM catalyst by the ion-exchange chromatography, heterogeneous high-pressure hydrogenation of the epimeric mixture is performed, usually catalyzed by $RaNi$ in aqueous solution [6–9]. Exceptionally, separation of D-mannitol from D-sorbitol can be achieved by crystallization [10]; separation of other epimeric polyols requires tedious chromatographic methods [11].

In such two-step process the final yield of the less available polyol, e.g. D-mannitol or D-lyxi-

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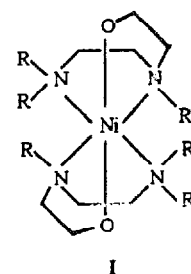
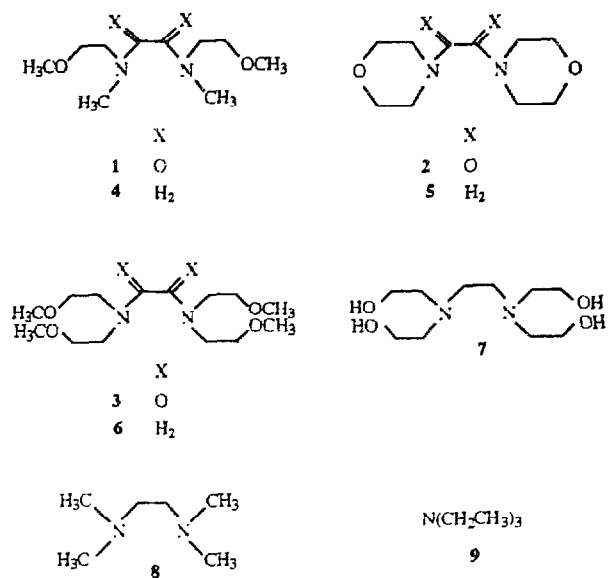
tol, is determined by the equilibrium reached after C(2) epimerization in the first step. This limitation can in principle be alleviated by shifting the equilibrium of C(2) epimerization either by changing the reaction medium, as observed for water-acetonitrile mixtures [5], or more conveniently by contemporaneous selective hydrogenation of the emerging C(2) epimer. This latter approach has not been attempted as yet, though based on the well known LeChattelier principle. It can be completed by employing two mutually compatible catalytic systems.



Epimerization is a reversible process: composition of the equilibrium mixture of two aldoses is governed by their relative stabilities under reaction conditions. Selective hydrogenation during epimerization of the less stable, and therefore more reactive aldose in the epimeric mixture, will result in complete conversion of the more stable aldose into C(2) epimeric alditol.

Accordingly, the convenient catalytic system, a single catalyst or a combination of two compatible catalytic species, would complete the conversion of the aldose **A** to the alditol **B** in a single pot. Some recent reports have addressed coupling of the reactions catalyzed by polyoxometalates, as e.g. oxidative dehydrogenation, acylation and coupling of hydrocarbons, combining an oxidative and reductive reaction in the one-pot catalytic process [12–15].

Molybdate ions seem unique among polyoxometalates in their property to catalyze C(2) epimerization. Tungstate ions are completely catalytically inactive, though CD and NMR studies have revealed formation of stable complexes with aldoses [3,16]. Complexes of same transition metals with bisnitrogen ligands were recently reported by Tanase et al. to promote C(2) epimerization of aldoses [17–23]. Because of the high molar ratio complex:substrate, usually 1:1, these complexes can hardly be regarded as the catalysts, however. Among a



Scheme 1.

number of metals and ligands tested [24,25,27], only the complexes of Ni(II), Ca(II), Co(II) and Sr(II) with *N,N,N'*-Me₃en (Me₃en: 1-(dimethylamino)-2-methylamino-ethane) and *N,N,N',N'*-Me₄en (Me₄en: 1,2-bis(dimethylamino)-ethane) have proven active. Moreover, they were studied in organic solvents exclusively, usually in methanol, because of the poor solubility of diamine complexes in water. In organic solvents, however, the aldoses are completely insoluble. Both aspects strongly limit productivity of this reaction, rendering such process a priori unattractive for commercial exploitation.

Searching for a 'comby' catalytic process, in this paper we report comparative study of epimerization of D-Glc and D-Man by some water soluble metal(II) complexes and molybdate complexes with bisnitrogen ligands 4–9 (see Scheme 1). In the following paper we

report comparative study of homogeneous hydrogenation of the same pair of epimeric aldoses [28].

2. Experimental

2.1. General

Melting points were determined on electrothermal melting point apparatus. ^1H - and ^{13}C -NMR spectra were obtained on JEOL FX 900FT and Varian XL-GEM 300 spectrophotometers; shifts are given in ppm downfield from TMS. GLC analyses were performed on a Hewlett Packard GC 5890 chromatograph with flame ionization detector (FID), HP 3396A integrator and capillary HP-17 column. HPLC analyses were performed with a Hewlett Packard 1050 pump equipped with an automatically controlled thermostat, HP 1047A refractometric detector and HP 3396A integrator.

2.2. Materials

D-Glc, D-Man (p.a., Fluka) were dried in vacuo for 24 h before use. Ammonium heptamolybdate tetrahydrate (NH_4) $\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (p.a., Aldrich), *N,N'*-ethylenediamine, methoxyacetylchloride, triethylamine, dimethoxyethylamine, oxalylchloride, morpholine, diethyloxalate, tetrakis-(2-methoxyethyl)-ethylenediamine (p.a., Fluka), $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$, SbCl_3 , (p.a., Kemika) were used as received. Redistilled water and p.a. organic solvents stored under nitrogen, were used in all experiments.

2.3. Preparation of the ligands

2.3.1. *N,N'*-Dimethyl-*N,N'*-bis(2'-methoxyacetyl)-ethylenediamide (1)

Methoxyacetyl chloride (25 g, 237 mmol), dissolved in toluene (50 ml) was added dropwise to the ice-cooled mixture of *N,N'*-ethylenediamine (10 g, 113 mmol) and triethylamine

(24 g, 237 mmol). The reaction mixture was stirred for 1 h at room temperature and progress of reaction was followed by GLC. It was then washed with 0.5 M sulfuric acid (3×50 ml) and the combined aqueous extracts were adjusted to $\text{pH} \geq 12$ with solid KOH. The crude product was extracted with dichloromethane (5×50 ml) and distilled, b.p. $200\text{--}230^\circ\text{C}/1$ mmHg, to afford 14 g (77.4%) of $\geq 90\%$ pure **1**. ^1H -NMR: 2.92 (s, 6H), 3.33 (s, 6H), 3.49 (s, 4H), 3.96 (d, 4H). ^{13}C -NMR: 34.34, 44.69, 59.22, 71.04, 169.85.

2.3.2. Bis-oxalylmorpholide (2)

The solution of diethyl oxalate (11 g, 75 mmol) and morpholine (16.5 g, 190 mmol) was heated under reflux for 7 days, and reaction was followed by GLC. On slow cooling to room temperature pure product has crystallized, it was obtained 8.96 g of **2** (52.4%, 96.1% GLC assay). ^{13}C -NMR: 41.25, 46.27, 66.31, 66.59, 167.73.

2.3.3. Bis-(dimethoxyethyl)-oxalylamide (3)

Starting from dimethoxyethylamine (10.5 g, 79 mmol) and triethylamine (7 g, 69 mmol), dissolved in toluene (250 ml), and oxalylchloride (2.2 g, 33 mmol) dissolved in toluene (50 ml), title compound was prepared as described for **1**. Crude product (9.5 g, 89.5%) exhibited 97.4% GLC purity, and was used in the next step without further purification. ^1H -NMR: 3.31 (s, 6H), 3.34 (s, 6H), 3.55–3.58 (m, 8H), 3.65–3.69 (m, 8H). ^{13}C -NMR: 44.60, 48.28, 58.58, 58.64, 69.99, 70.88, 165.52.

2.3.4. Preparation of ethylenediamines 4–6, general procedure

Diamides **1–3** (40 mmol) were dissolved in THF (50 ml), and resulting solution was added under ice-cooling to the stirred suspension of LiAlH_4 (4.6 g, 120 mmol) in THF. The reaction mixture was then warmed up to 50°C , and reaction monitored by GLC. After completed conversion crushed ice was added, and precipitate separated by filtration. Filtrate was washed with 0.5 M sulfuric acid (3×50 ml), combined

aqueous extracts were made alkaline, $\text{pH} \geq 12$, with solid KOH. Crude products were extracted with dichloromethane (5×50 ml) and were either distilled under reduced pressure or recrystallized.

2.3.5. *N,N'*-Dimethyl-*N,N'*-bis(2'-methoxyacetyl)-ethylenediamine (4)

Crude product (9.68 g, 84.5%) was distilled at $80^\circ\text{C}/3$ mmHg, affording 4.7 g of pure 4, 94.7% GLC assay. $^1\text{H-NMR}$: 2.29 (s, 6H), 2.55 (s, 4H), 2.59 (t, $J = 5.7$ Hz, 4H), 3.35 (s, 6H), 3.48 (t, $J = 6.0$ Hz, 4H). $^{13}\text{C-NMR}$: 42.73, 55.46, 56.91, 58.45, 70.31.

2.3.6. 1,2-Dimorpholino-ethane (5)

Crude product was crystallized from dichloromethane affording 4.4 g (52.4%) of crystals, m.p. $72.8\text{--}73.8^\circ\text{C}$, GC assay 97.5%. $^1\text{H-NMR}$: 2.44 (t, $J = 4.8$ Hz, 8H), 2.46 (s, 4H), 3.66 (t, $J = 4.8$, 8H). $^{13}\text{C-NMR}$: 53.89, 55.85, 66.69.

2.3.7. *N,N,N',N'*-Tetramethoxyethyl-ethylenediamine (6)

The crude, oily product (7.7 g, 88.9%), was distilled at $150^\circ\text{C}/0.4$ mmHg, to afford 3.6 g (47%) of 6, 94.1% GLC assay. $^1\text{H-NMR}$: 2.68 (s, 4H), 2.73 (t, $J = 6.0$ Hz, 8H), 3.32 (s, 12 H), 3.46 (t, $J = 6.0$ Hz, 8H). $^{13}\text{C-NMR}$: 52.90, 54.21, 58.57, 70.93.

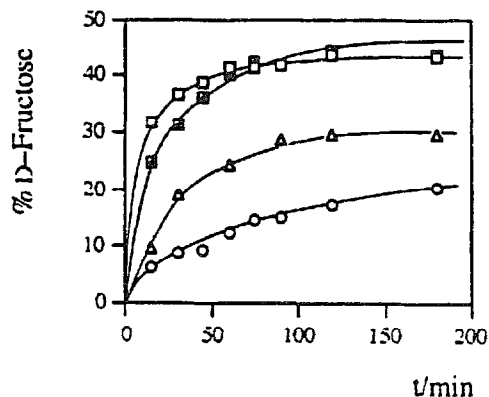


Fig. 1. Progress curve for the isomerization of D-Glc to D-fructose catalyzed by complexes: □ [Ni(II)-4], ○ [Ni(II)-5], ■ [Ni(II)-6], △ [Ni(II)-7] in water at 100°C .

Table 1

C(2) epimerization of D-Glc catalyzed by [Ni(II)-*N,N*-diamine] complexes, in water at 100°C and in methanol at 60°C ^a

| Complex | Equilibrium mixture | | | | | |
|------------|----------------------------|-------|------------|------------------------------|-------|------------|
| | water, 100°C | | | methanol, 60°C | | |
| | D-Glc | D-Man | D-Fructose | D-Glc | D-Man | D-Fructose |
| [Ni(II)-4] | 44.2 | 12.0 | 43.8 | 30.8 | 12.7 | 56.6 |
| [Ni(II)-5] | 81.8 | 3.1 | 15.0 | 86.3 | 10.4 | 3.3 |
| [Ni(II)-6] | 45.9 | 12.1 | 42.0 | 64.3 | 4.8 | 30.9 |
| [Ni(II)-7] | 57.7 | 10.0 | 29.7 | | | |

^a Molar ratio of D-Glc:Ni(II):diamine was 1:1:2; reaction time: 90 min.

2.4. Catalytic C(2) epimerization

All experiments for the determination of progress curves were repeated twice.

C(2) epimerization was performed in a home-made double-walled, 50 ml glass reactor, thermostated by Haake L circulator thermostat with silicon oil as the heating medium. The aldose (1 mmol) was dissolved in water or methanol and the inorganic salt (1 mmol) and diamine 4–9 (2 mmol) were added to the solution. Samples of the reaction mixture (0.2 ml) were taken at various time intervals and diluted by water (0.6 ml). The progress of reaction was monitored by HPLC on Aminex HPX-87C column (300×7.8 mm) (Bio-Rad), thermostated at 85°C . Redistilled water was used as the eluant at flow rate of 0.8 ml/min. Under these conditions the retention times were as follows: HM 5.30 min, D-Glc 7.60 min, D-Man 9.23 min, D-fructose 10.22 min.

3. Results and discussion

In the present study we wished to expand the range of the complexes with bidentate nitrogen ligands that promote C(2) epimerization in organic solvents, reported by Tanase et al. [17,23], to those with additional hydroxy groups or oxygen atoms in order to obtain water-soluble complexes with transition metals as Cu(II), Ni(II),

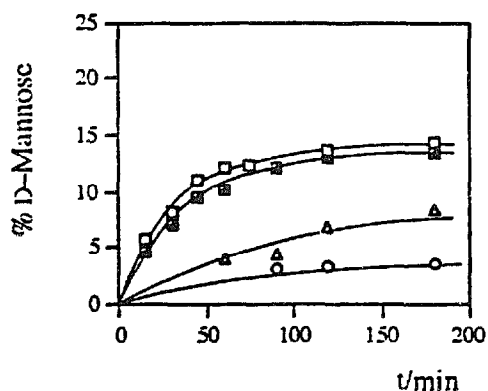


Fig. 2. Progress curve for the C(2) epimerization of D-Glc to D-Man catalyzed by complexes: □ [Ni(II)-4], ○ [Ni(II)-5], ▣ [Ni(II)-6], △ [Ni(II)-7] in water at 100°C.

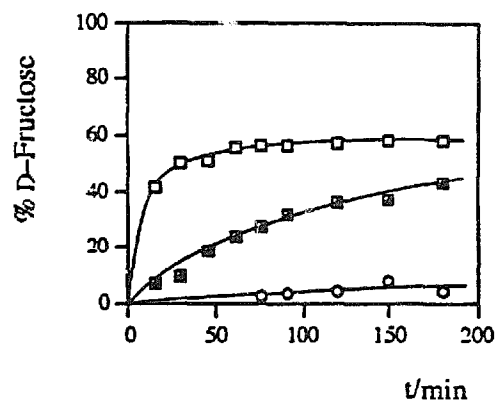


Fig. 3. Progress curve for the isomerization of D-Glc to D-fructose catalyzed by complexes: □ [Ni(II)-4], ○ [Ni(II)-5], ▣ [Ni(II)-6] in methanol at 60°C.

Co(II) and Cd(II). Such complexes were expected to epimerize aldoses at catalytic concentrations in aqueous solution, where high concentrations of sugars can be achieved. For comparison, the same ligands are combined with HM ions in the expectation of obtaining particularly selective catalysts.

Initiating this project, water-soluble Ni(II) complexes with the ligands 4–7 have been examined. Epimerization of D-Glc was performed in water at 100°C, and – to compare the results with those of Tanase et al. [26,27] also in methanol at 60°C. In all experiments molar ratio D-Glc:Ni(II):ligand was 1:1:2, as used by Tanase et al. Final conversions, reached after 90 min, are presented in the Table 1, and progress curves in the Figs. 1–4.

HPLC monitoring surprisingly revealed isomerization of D-Glc to D-fructose as the primary process in both solvents, and C(2) epimerization as the slower one. This result can be explained by inactivation of Ni(II) on complexation to the ligands 4–7, which can form hexacoordinated complexes of the general formulae I. Klufers reported formation of neutral complexes of Cu(II) and Pd(II) with polyols in aqueous solutions [29]. Analogously, the OH and NH group, or N atom, in the ligands 4–8 may be used by the metal to form π or donor bonds, or a combination of the two, depending on the oxophilicity of the bound metal.

Since deactivation of Ni(II) complexes could be consequence of the low metal:ligand ratio, epimerization was performed at a D-Glc:metal:ligand ratio of 1:1:1, Fig. 5. No formation of D-Man was observed, the only product was D-fructose, formed at approximately the same rate as with the 1:2 metal:ligand ratio. The test of ligand 7 in the absence of the metal ions, for both directions of epimerization, at an aldose:ligand molar ratio of 1:2, resulted in the processes presented in Figs. 6 and 7. Isomeric D-fructose and C(2) epimeric aldose were formed from both substrates, though in somewhat different proportions. There was 52.3% of D-Glc, 10.3% of D-Man, and 37.6% of D-fructose in the equilibrium mixture reached from D-Glc, but

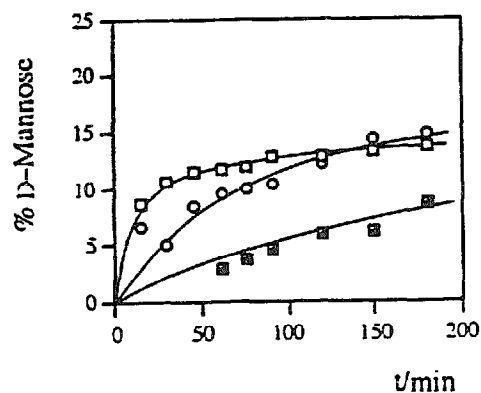


Fig. 4. Progress curve for the C(2) epimerization of D-Glc to D-Man catalyzed by complexes: □ [Ni(II)-4], ○ [Ni(II)-5], ▣ [Ni(II)-6] in methanol at 60°C.

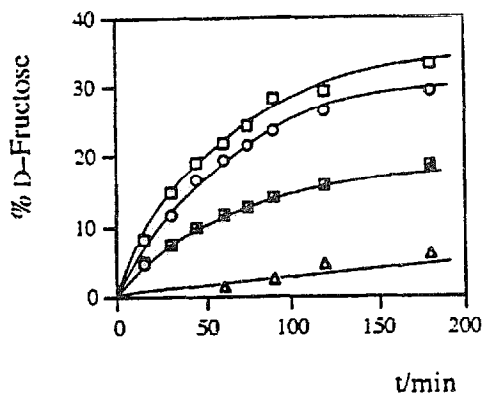


Fig. 5. Progress curve for the C(2) epimerization of D-Glc catalyzed by \square [Ni(II)-4], \circ [Ni(II)-5], \blacksquare [Ni(II)-6], \triangle [Ni(II)-7] complexes in water at 100°C; molar ratio of D-Glc:Ni(II):diamine is 1:1:1.

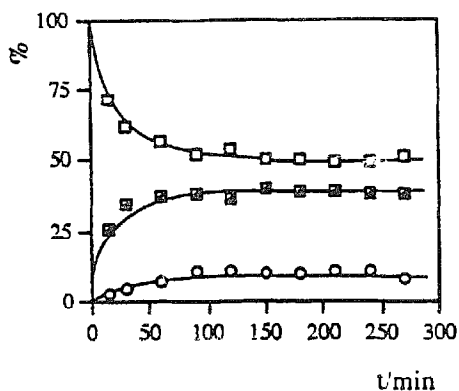


Fig. 6. Progress curve for the C(2) epimerization of D-Glc catalyzed by ligand 7 in water at 100°C; molar ratio of D-Glc:7 is 1:2; \square D-Glc, \circ D-Man, \blacksquare D-fructose.

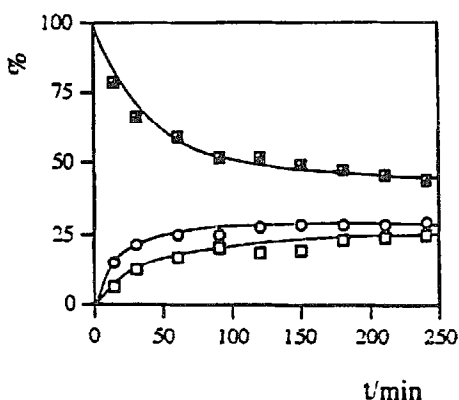


Fig. 7. Progress curve for the C(2) epimerization of D-Man catalyzed by ligand 7 in water at 100°C; molar ratio of D-Man:7 is 1:2; \blacksquare D-Man, \square D-Glc, \circ D-fructose.

Table 2

C(2) epimerization of D-Glc catalyzed by [(Mo(VI)-N-ligand)] complexes in water at 100°C

| Complex | t (min) | D-Glc:D-Man |
|---------|-----------|-------------|
| AHM | 15 | 62:38 |
| [Mo-4] | 270 | 70:30 |
| [Mo-5] | 270 | 76:24 |
| [Mo-6] | 270 | 92:8 |
| [Mo-7] | 270 | 94:6 |
| [Mo-8] | 15 | 70:30 |
| [Mo-9] | 15 | 62:38 |

44.4% D-Man, 24.9% D-Glc, and 28.7% of D-fructose in the equilibrium mixture reached from D-Man. This outcome reveals that the free ligand 7 epimerizes D-Man faster than D-Glc, as observed also with HM [2], and that both aldoses isomerize into D-fructose, both processes being obviously base-catalyzed.

To conclude this section, water soluble complexes of Ni(II), Cu(II), Co(II) and Cd(II) with bisnitrogen ligands proved non-selective in C(2) epimerization, catalyzing contemporaneous isomerization of both aldoses to D-fructose.

In the second part of this study we prepared in situ complexes of AHM by adding equimolar quantities of the ligands 4–9. The exact stoichiometries of $[\text{Mo(VI)}-(N,N\text{-diamine})_n]$ and $[\text{Mo(VI)}-(N\text{-alkylamine})_n]$ complexes have not been determined.

Table 2 presents the ratios of D-Glc/D-Man achieved with the single complex. Fig. 8 shows the progress curves of epimerization at 100°C.

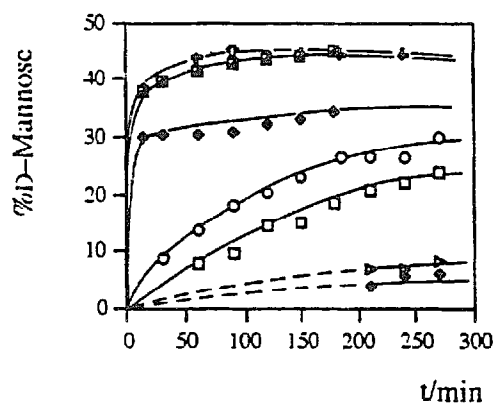


Fig. 8. Progress curve for the C(2) epimerization of D-Glc catalyzed by \blacksquare AHM, \circ [Mo-4], \square [Mo-5], \triangleright [Mo-6], \blacklozenge [Mo-7], \blacklozenge [Mo-8], $+$ [Mo-9] complexes in water at 100°C; molar ratio of D-Glc:[(Mo(VI)-ligand)] is 10:1.

Table 3
C(2) epimerization of D-Glc catalyzed by [Mo-8] complex in water at 100°C

| Complex | Molar ratio of D-Glc:complex | t (min) | D-Glc:D-Man |
|---------|------------------------------|---------|-------------|
| AHM | 278:1 | 45 | 70:30 |
| [Mo-8] | 278:1 | 270 | 80:20 |
| [Mo-8] | 139:1 | 270 | 72:28 |
| [Mo-8] | 70:1 | 180 | 70:30 |
| [Mo-8] | 10:1 | 15 | 70:30 |

and at 10:1 molar ratio D-Glc:[Mo(VI)-ligand]. The results reveal nearly equal activity of the complexes [Mo-8], [Mo-9], and AHM. The efficacy of the complexes [Mo-4] and [Mo-5] is notably lower, however, the equilibrium being reached after 270 min, while the complexes [Mo-6] and [Mo-7] proved nearly inactive. In all experiments the aldose:Mo(VI) ratio was 10:1, i.e. ten times higher than that used by Tanase [27] with Ni(II) complexes of bisnitrogen ligands, but still much lower than in the catalytic epimerizations with AHM [4,5]. We therefore examined the effect of the aldose:[Mo-8] ratio on the rate of epimerization. The data collected in Table 3 and Fig. 9 show that the catalytic efficacy of [Mo-8] is significantly lower than that of AHM; ca. 70:30 D-Glc:D-Man equilibrium is still reached, though after notably longer reaction times.

Diminished catalytic efficacy of bidentate

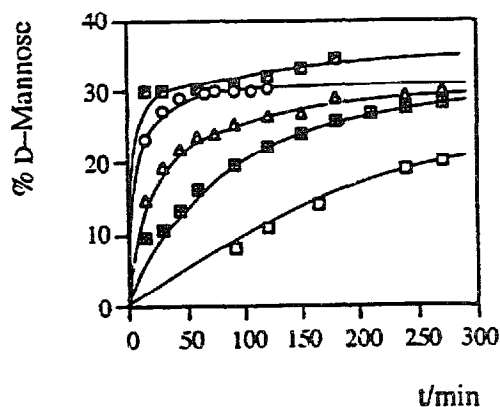


Fig. 9. Progress curve for the C(2) epimerization of D-Glc catalyzed by [Mo-8] complexes at molar ratio of Glc:[Mo-8]: □ 278:1, ▣ 139:1, △ 70:1, ⋈ 10:1, and AHM at molar ratio of ○ 278:1, in water at 100°C.

ligands presented in Table 2 can be explained by coordination of depolymerized polymolybdate ions to nitrogen ligand. Ligands 4–7, which possess additional hydroxy or methoxy groups presumably coordinate to Mo(VI) by both heteroatoms forming catalytically less active species, that have largely lost the coordinating ability for aldoses.

In conclusion, the accumulated data accentuated AHM as the unique, highly specific catalyst for C(2) epimerization of aldoses. We therefore entered the study of homogeneous hydrogenation catalysts described in the next paper [28], expecting their compatibility with AHM catalyzed epimerization.

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References

- [1] B. Klaić, Z. Raza, M. Sanković, V. Šunjić, *Helv. Chim. Acta*, 70 (1987) 39.
- [2] M. Sanković, Sh. Emimi, S. Rusman, V. Šunjić, *J. Mol. Catal.*, 61 (1990) 247.
- [3] G. Snatzke, J. Guo, Z. Raza, V. Šunjić, *Croat. Chem. Acta*, 64 (1991) 501.
- [4] S. Kolarić, M. Gelo, M. Sanković, V. Šunjić, *J. Mol. Catal.*, 79 (1993) 365.
- [5] S. Kolarić, M. Gelo, V. Šunjić, *J. Mol. Catal.*, 89 (1994) 247.
- [6] F.B. Bizhanov, D.V. Sokolskii, R.B. Drozdova, *Dokl. Akad. Nauk SSSR*, 269 (1983) 859.
- [7] M. Makkee, A.P.-G. Kieboom, H. van Bekkum, *Carbohydr. Res.*, 138 (1985) 225.
- [8] R. Verma, J.K. Gehlawat, *J. Chem. Technol. Biotechnol.*, 46 (1989) 295.
- [9] G. Darsow (for Bayer AG) *Ger. Offen.* 3934457, *Chem. Abstr.* 114 (1992) 247688.
- [10] F. Matsunaga, E. Kato, T. Kimura, Y. Isato, *Eur. Pat. Appl.* 224 625 (1985); *Chem. Abstr.* 107 (1987) 116962.
- [11] V. Bilik, M. Matulova, I. Knezek, *Chem. Zvesti.* 44 (1990) 703.

- [12] R.C. Chambers, C.L. Hill, *J. Am. Chem. Soc.* 112 (1990) 8427.
- [13] M. Misono, *Catal. Rev.-Sci. Eng.* 29 (1987) 269.
- [14] R.F. Renneke, M. Kadhodayan, M. Pasquali, C.L. Hill, *J. Am. Chem. Soc.* 113 (1991) 8357.
- [15] S. Daryush, C.L. Hill, *J. Am. Chem. Soc.* 115 (1993) 4649.
- [16] S. Chapelle, J.F. Verchere, *Inorg. Chem.* 31 (1992) 648.
- [17] S. Takizawa, H. Sugita, S. Yano, S. Yoshikawa, *J. Am. Chem. Soc.* 102 (1980) 7968.
- [18] S. Yano, S. Takizawa, S. Sugita, H. Takahashi, T. Tsubomora, H. Shioi, S. Yoshikawa, *Carbohydr. Res.* 142 (1985) 179.
- [19] T. Tsubomura, S. Yano, K. Toriuma, T. Ito, S. Yoshikawa, *Bull. Chem. Soc. Japan*, 57 (1984) 1833.
- [20] T. Tsubomura, S. Yano, K. Toriuma, T. Ito, S. Yoshikawa, *Inorg. Chem.* 24 (1985) 3218.
- [21] H. Shioi, S. Yano, S. Yoshikawa, K. Toriumi, T. Ito, *J. Chem. Soc. Chem. Commun.* (1983) 201.
- [22] S. Yano, Y. Sakai, K. Toriuma, T. Ito, S. Yoshikawa, *Inorg. Chem.* 24 (1985) 498.
- [23] K. Ishida, S. Yano, S. Yoshikawa, *Inorg. Chem.* 25 (1986) 3552.
- [24] T. Tanase, K. Kurihara, S. Yano, K. Kobayashi, T. Sakurai, S. Yoshikawa, *J. Chem. Soc., Chem. Commun.* (1985) 1562.
- [25] T. Tanase, F. Shimizu, S. Yano, S. Yoshikawa, *J. Chem. Soc., Chem. Commun.* (1986) 1001.
- [26] Tanase, F. Shimizu, M. Kuse, S. Yano, S. Yoshikawa, M. Hidai, *J. Chem. Soc., Chem. Commun.* (1987) 659.
- [27] T. Tanase, F. Shimizu, M. Kuse, S. Yano, M. Haidi, S. Yoshikawa, *Inorg. Chem.* 27 (1988) 4085.
- [28] S. Kolarić, V. Šimjić, *J. Mol. Catal.* (1996) this issue.
- [29] P. Klufers, J. Schuhmacher, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 685.