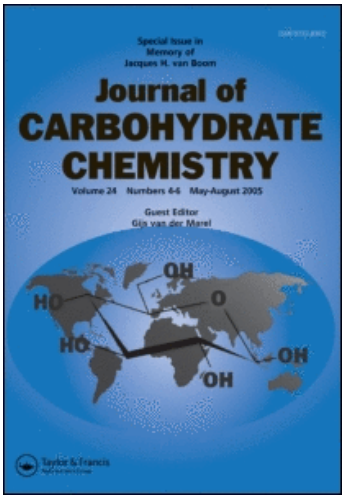

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Oxidation Studies of Carbohydrates Using Molecular Oxygen and a Bismuth-Ruthenium Oxide Catalyst

Stefan J. H. F. Arts[a]; Fred van Rantwijk[a]; Roger A. Sheldon[a]
[a] Laboratory for Organic Chemistry and Catalysis, Delft University of Technology, Delft, BL, The Netherlands

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OXIDATION STUDIES OF CARBOHYDRATES USING MOLECULAR OXYGEN AND A BISMUTH-RUTHENIUM OXIDE CATALYST

Stefan J.H.F. Arts, Fred van Rantwijk and Roger A. Sheldon*

Laboratory for Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

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ABSTRACT

The oxidation of *trans*-1,2-cyclohexanediol, methyl α-D-glucopyranoside and β-cyclodextrin has been studied, using a heterogeneous oxidation system in water at 50-75 °C. Molecular oxygen at 15-20 bar was used as the oxidant, in combination with a bismuth-rich ruthenium pyrochlore oxide as the catalyst. Both oxidative cleavage of the vicinal diols and oxidation of the primary hydroxyl groups occurred. HPLC and ^{13}C NMR were used to analyse the complex product mixtures. The oxidation method is successful for glycol cleavage in small carbohydrates but not for polysaccharides.

INTRODUCTION

Nowadays polyacrylates are used as cobuilders in detergent formulations. Because the biodegradability of these compounds is very poor,[1] substitutes are needed that combine good ion sequestering properties with easy degradation in sewage and waste water. It has been reported[2] that dicarboxylic starch shows very good performance as a cobuilder in detergent formulations. However, no economically viable process is yet available to produce dicarboxylic starch in bulk quantities. Environmental and economic considerations exclude the use of metal oxidants in stoichiometric amounts, as well as oxidants like periodate.

From an industrial viewpoint, the most interesting system for starch oxidation is molecular oxygen in an aqueous medium. Unfortunately, most oxidations of hydroxyl

groups reported in the literature involve the use of non-aqueous media that can not be applied to starch. One of the few examples of oxygenation in an aqueous alkaline medium, has been reported by Felthouse.[3,4] Alcohols such as 2-butanol, 1,6-hexanediol and *trans*-1,2-cyclohexanediol were oxidised to the corresponding ketone and diacids over expanded lattice ruthenium pyrochlore oxide catalysts with the general composition[5] $A_{2+x}Ru_{2-x}O_{7-y}$ (A = Pb, Bi; $0 < x < 1$; $0 < y \leq 0.5$). He also reported[6] the oxidation of methyl α-D-glucopyranoside using a RuBi pyrochlore catalyst in 1.26M CsOH solution. The products formed were not isolated but structures were assigned on basis of HPLC (ion exchange chromatography with pulsed amperometric detection) and ^{13}C NMR data from product mixtures. The results presented were therefore somewhat ambiguous but promising and we started investigations in this field.

Earlier attempts[7,8] to apply the lead-ruthenium oxide catalysts with oxygen to carbohydrates remained unsuccessful. This pyrochlore oxide catalyst[9] proved to be effective when hypochlorite was used[8,10] as the oxidant. However, we now report the successful oxidative cleavage of carbohydrates using a related pyrochlore oxide catalyst based on ruthenium and bismuth[11] with molecular oxygen as the oxidant.

RESULTS AND DISCUSSION

Catalyst Preparation. Five species of the expanded lattice lead- or bismuth-rich ruthenium pyrochlore oxide catalyst were prepared according to methods described[11] by Horowitz. This preparation yields a high surface area and thus[4] high activity. The ruthenium lead pyrochlore oxide [RuPb (9,6,3)] and ruthenium lead on active carbon [RuPb (9,6,3)/C] were prepared by precipitation in an aqueous solution of 9 M KOH and consecutive stirring in solutions with decreasing KOH concentrations of 9, 6 and 3 M. Ruthenium bismuth pyrochlore oxide [RuBi (9,6,3)] and ruthenium bismuth on active carbon [RuBi (9,6,3)/C], were synthesised in an analogous manner. One of the ruthenium bismuth pyrochlore oxides [RuBi (12)] was prepared by stirring in an aqueous solution of 12 M KOH only.

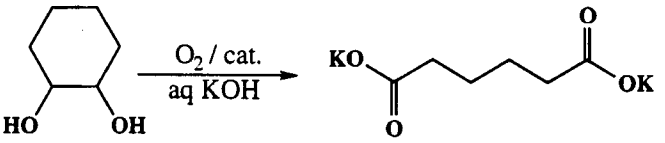
The five catalysts were characterised using several techniques:

-Inductively coupled argon plasma - orbital emission spectroscopy (ICP-OES) for determination of the ratio of ruthenium to lead or bismuth;

-Gas adsorption -desorption experiments for determining the multi-point BET surface areas;

-Powder X-ray diffraction (XRD) to analyse the crystallinity of the material.

The results were in accordance with Felthouse:[4] ICP-OES showed that all catalysts had the correct Ru/Pb or Ru/Bi ratio of the pyrochlore formula, the BET surface of the



Scheme 1

catalysts was between 50 and 150 m^2g^{-1}, the RuBi (9,6,3) catalyst having the largest surface area; XRD showed a pyrochlore structure but also some amorphous material was present.

***Trans*-cyclohexanediol**. Cleavage of *trans*- 1,2-cyclohexanediol was chosen as the first test reaction (Scheme 1) simulating the glycol cleavage of the pyranoside rings of carbohydrates and using the above mentioned five catalysts.

Good results were obtained with ruthenium bismuth pyrochlore oxide [RuBi (9,6,3)] and a catalyst prepared likewise on active carbon [RuBi (9,6,3/C]. Fig. 1 and 2 depict the results obtained with RuBi (9,6,3). The reaction mixture obtained with RuBi (9,6,3)/C was always slightly yellow, probably because of the oxidation of some of the active carbon.

The ruthenium bismuth pyrochlore oxide prepared in 12 M KOH [RuBi (12)] had a lower surface area. It was much less active and the oxidations were insufficiently selective. The ruthenium lead oxide and ruthenium lead oxide-on-charcoal were less selective than the ruthenium bismuth catalysts, affording more than double the amounts of formate and carbonate by chain degradation.

The shape of the lines in Fig. 1 suggests that the catalyst was not deactivated during the oxidation reaction. Indeed, the catalyst could be recovered by centrifugation and reused at least ten times without loss of activity.

In agreement with Felthouse,[3,4] we found that the selectivity decreased with increasing temperature. On raising the temperature from 50 to 75 °C, the rate of oxidation increased twofold but relatively more side products such as formate were observed (Fig. 2). After complete conversion of *trans*-cyclohexanediol no further formation of formic acid was observed during 50 hours, demonstrating that adipic acid was stable under the reaction conditions. (Note: the higher amount of adipic acid produced in Fig. 2 is due to the higher conversion.)

In order to investigate the dependence of the reaction rate on the concentration of hydroxyl ions, two experiments were performed with different amounts of KOH added.

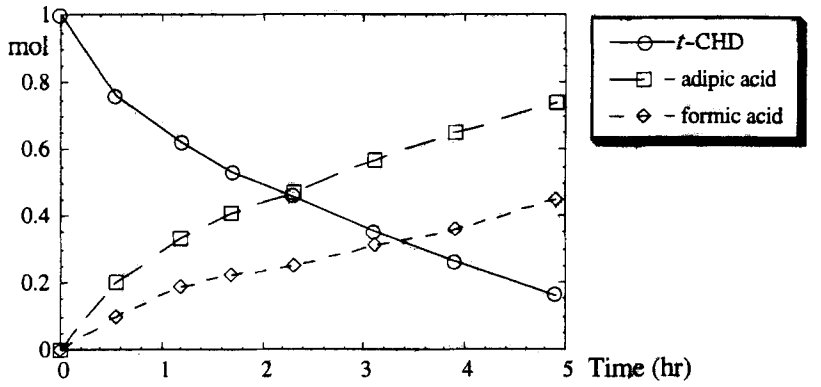


Fig. 1 Oxidation of *trans*-1,2-cyclohexanediol (*t*-CHD) with ruthenium bismuth pyrochlore oxide (RuBi 9,6,3) and O_2 (20 bar) at 50 °C.

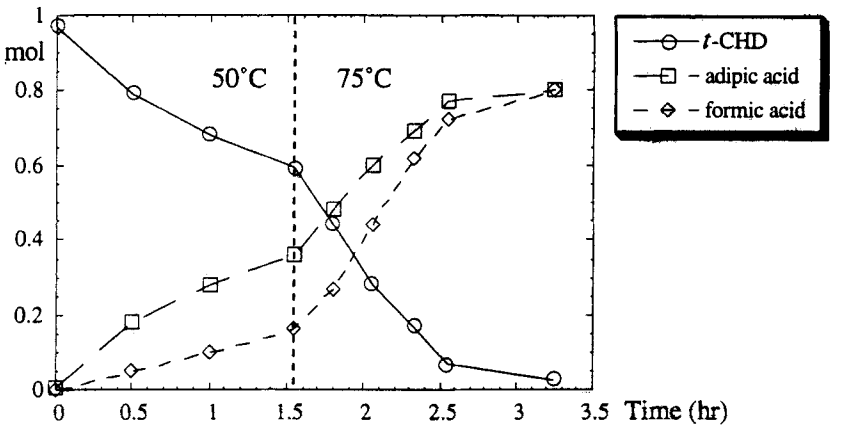
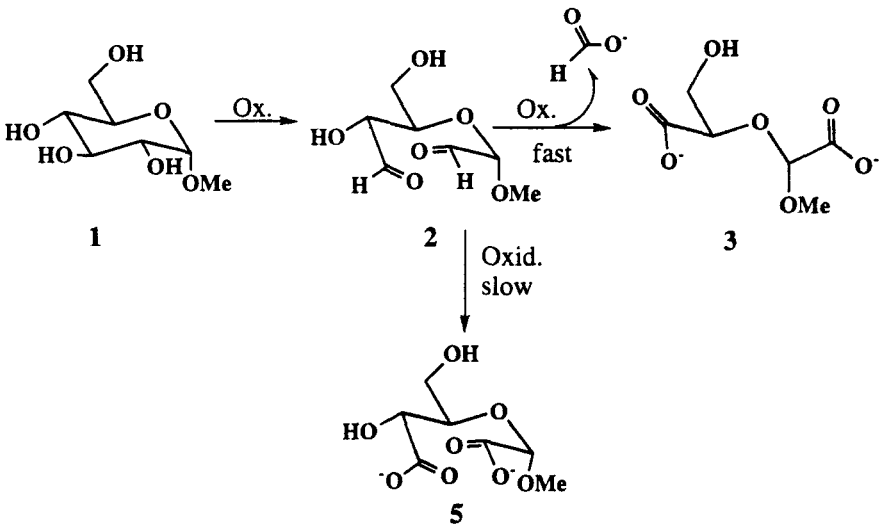


Fig. 2 Oxidation of *trans*-1,2-cyclohexanediol (*t*-CHD) with ruthenium bismuth pyrochlore oxide and O_2 (20 bar) at 50 and 75 °C.

The results with concentrations of 1.5 M and 0.5 M (6 respectively 2 equivalents of KOH per produced carboxylate) were practically identical. Hence we conclude that the high burden of inorganic salt in the reaction as performed by Felthouse[4] can be significantly reduced.

From the tests performed, we also conclude that RuBi (9,6,3) is the best catalyst for the cleavage reaction, affording the highest selectivities.

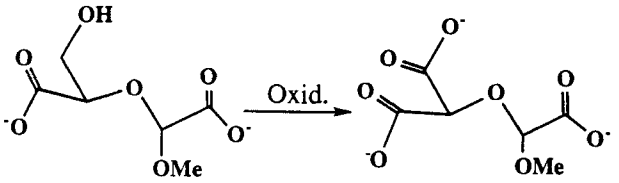


Scheme 2

Methyl α-D-glucopyranoside. In order to compare the relative reactivities of this catalytic system towards the primary and secondary hydroxyl functions present in carbohydrates, methyl α-D-glucopyranoside (**1**) was chosen as a model. Oxidation of (**1**) was faster than that of *trans*-1,2-cyclohexanediol under similar conditions over the ruthenium bismuth oxide catalyst which may be due to the higher polarity of the substrate, resulting in a better contact with the polar catalyst surface. All carboxylate reaction products were isolated by preparative anion exchange chromatography and identified by NMR. The C(2)-C(3) dialdehyde intermediate (**2**) (Scheme 2) could not be isolated but the formation of formate and the C(2)-C(4) dicarboxylate (**3**) could only result from this intermediate. Also the isolation from the reaction mixtures of small amounts of the dipotassium (*R*)-3-*O*-[(*R*)-carboxylato-(methoxy)-methyl] (*R*)-2,4-dihydroxybutanoate (**5**) formed by oxidation of the aldehyde groups of **2** was consistent with the intermediate formation of **2**.

Glycol cleavage:

Oxidative cleavage of the C(2)-C(3) bond in **1** resulted in formation of the dialdehyde (**2**) as the initial product (Scheme 2). Its concentration remained low (<5%), probably because of the facile oxidative decarboxylation of the unprotected C(4) forming dipotassium (*R*)-2-*O*-[(*R*)-carboxylato-(methoxy)-methyl] 3-hydroxypropanoate (**3**) together with formate.



3 4

Scheme 3

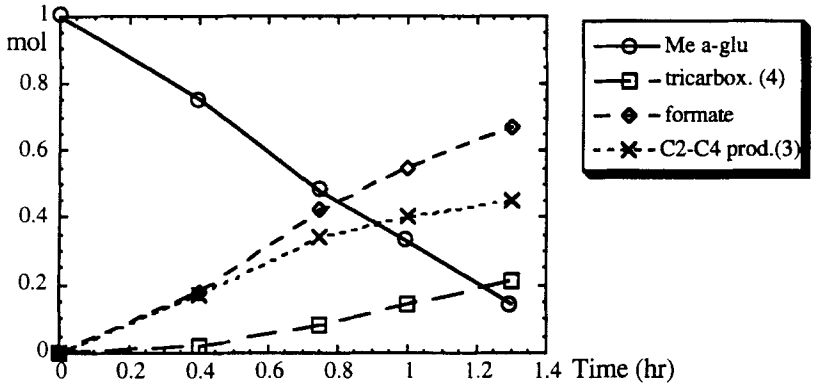
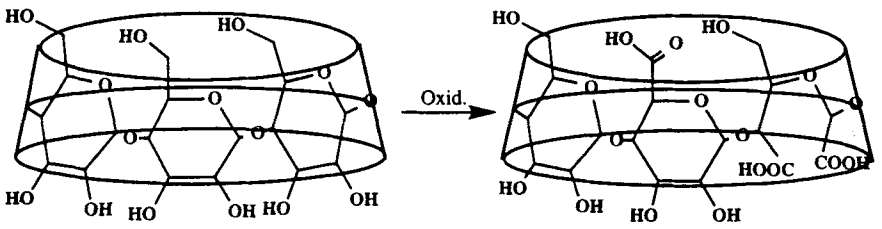


Fig. 3 Oxidation of methyl α-D-glucopyranoside: ruthenium bismuth oxide and O_2 (20 bar), 70 °C.

The amount of formate matched (Fig. 3) the total amount of **3** and **4** which both have lost the C(4) carbon of the original pyranoside ring. The amount of C(2)-C(3) dicarboxylate (**5**) was low (<3%).

Oxidation of the primary hydroxyl groups:

The tripotassium salt of 2-*O*-[(*R*)-carboxylato-(methoxy)-methyl]-propanedioic acid (**4**) became a significant product at high conversions. Its late appearance suggests that **4** results from oxidation of the primary OH group of **3** (Scheme 3), rather than from glycol cleavage of potassium 1-*O*-methyl glucuronate, which was present in the reaction mixture in only minor amounts (1-3%). Hence we conclude that the oxidation of the primary hydroxyl group is significantly slower than diol cleavage.



Scheme 4

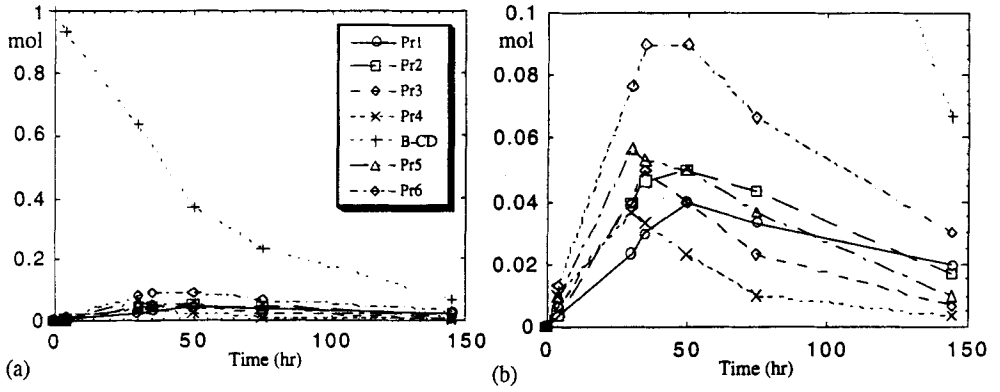


Fig. 4 Oxidation of β-cyclodextrin with RuBi oxide and O_2 (20 bar, 70 °C)

The data obtained from NMR analysis were used for monitoring the course of the reaction by HPLC (Fig. 3)

β-cyclodextrin. Encouraged by the successful oxidation of methyl α-D-glucopyranoside we diverted our attention to β-cyclodextrin, a model compound more closely resembling amylose (Scheme 4).

β-Cyclodextrin reacted significantly slower than *trans*-1,2-cyclohexanediol and methyl α-D-glucopyranoside (Fig. 4a). Using RuBi (9,6,3) and RuBi (9,6,3)/C as catalysts, a large number of products were formed as shown in Fig. 4b.

Analysis by HPLC (Dionex column) and ^{13}C NMR indicated that hydrolysis of β-cyclodextrin and not its direct oxidation was involved in the formation of these products. At higher conversions (> 70%) they were converted to formate and carbonate, as shown by HPLC (organic acids column) and ^{13}C NMR.

The crude reaction mixture obtained after 35 hours was desalinated by ultra filtration and subsequently most of the remaining β-cyclodextrin was removed by crystallisation.

^{13}C NMR analysis of the final mixture showed considerable broadening of the pyranoside signals, indicating intact but non-equivalent pyranoside rings and a low degree of oxidised pyranoside units; furthermore a minor amount of carboxylic groups could be observed in the products.

Control experiments showed that no reaction occurred in the absence of oxygen, meaning that neither hydrolysis or oxidation were possible without oxygen. This result indicated that under basic conditions deprotonation of some of the OH groups in β-cyclodextrin took place, followed by oxidation of the resulting alcoholates with oxygen. In an experiment without catalyst the same degradation products of β-cyclodextrin were formed, but the rate of the reaction was reduced by almost a factor four.

We conclude that β-cyclodextrin is not selectively oxidised with oxygen using the ruthenium bismuth pyrochlore oxide catalyst and that initial hydrolysis is the major reaction pathway. The smaller reaction products originating from hydrolysis of β-cyclodextrin are oxidised faster than β-cyclodextrin itself, thus precluding the formation of the desired polycarboxylates in any significant yield.

This problem appears to be inherent to a heterogeneous catalytic system for liquid phase oxidation of large substrate molecules. Preliminary experiments showed that initial hydrolysis was also the major pathway when linear maltodextrins were used as the substrate. Therefore, we conclude that ruthenium pyrochlore oxide catalysts are only suitable for the oxidation of small carbohydrates and not for polysaccharides such as starch.

EXPERIMENTAL

Catalyst Preparation and Analysis. All catalysts were prepared according to methods of Horowitz.[11] In a typical catalyst synthesis, 2.42 g (5.0 mmol) of $Bi(NO_3)_3.5H_2O$ was dissolved in 50 mL of concentrated HNO_3 solution and 100 mL of water to which was added 9.87 g (5.0 mmol) of $Ru(NO_3)_3$ solution. This solution was slowly added to an aqueous 600 mL 9 M KOH solution held at 75 °C and a black precipitate was immediately formed. The suspension was stirred at 75 °C for 1 day through which oxygen was continuously bubbled. After centrifugation and decantation the remaining solid was suspended in 600 mL of 6M KOH solution at 75 °C and stirred and bubbled with oxygen for one more day. After another centrifugation, the precipitate was finally stirred and bubbled with oxygen for two days in 600 mL of 3M KOH solution at 85 °C. The catalyst was recovered by centrifugation and washed with water to remove the residual KOH.

Determination of the BET surface area showed that the RuPb (9,6,3) had a comparatively low surface of 35 m^2g^{-1}, while the RuBi (9,6,3) had a large area of 158 m^2g^{-1}. RuBi (12M) had a surface area of 97 m^2g^{-1}. The catalysts had only meso and no micro pores. The ratio of Ru/Bi and Ru/Pb as determined by ICP-OES was according to the pyrochlore formula: $A_{2+x}Ru_{2-x}O_{7-y}$ (A = Pb, Bi; $0 < x < 1$; $0 < y \leq 0.5$). RuPb (9,6,3) and RuPb (9,6,3)/C had ratios of, respectively, $Pb_{2.79}Ru_{1.21}$ and $Pb_{2.82}Ru_{1.18}$. The RuBi (9,6,3) had $Bi_{2.81}Ru_{1.19}$, RuBi (12M) had a ratio of $Bi_{2.74}Ru_{1.26}$ while RuBi (9,6,3)/C was $Bi_{2.90}Ru_{1.10}$. The XRD data suggested a pyrochlore structure for the RuPb (9,6,3) catalyst while the RuBi catalysts had a pyrochlore spectrum but also contained some amorphous material (broadening of the lines).

General Procedures for the Oxidation Experiments. All experiments were performed in a 300 mL Hastalloy C stainless steel Parr autoclave and reaction mixtures were stirred with a propeller fan at 1500 rpm. Air was replaced with oxygen by flushing before pressurising the autoclave. At suitable time intervals aliquots of 2 mL were taken for analysis.

Samples of *trans*-1,2-cyclohexanediol and methyl α-D-glucopyranoside were analysed by HPLC on a system consisting of a Millipore-Waters 590 pump, a Perkin-Elmer ISS-100 autosampler, a Spark Holland column thermostat SpH 99, a Shimadzu SPD-6A UV spectrophotometric detector, a Shodex RI SE-51 refractive index detector and a Spectra-Physics SP4270 integrator.

The oxidation of *trans*-1,2-cyclohexanediol was monitored using a 300x7.8 mm Rezex organic acids column from Phenomenex at 60 °C, with aqueous 0.01 M trifluoroacetic acid (0.6 mL/min.) as the mobile phase. The same system was used for methyl α-D-glucopyranoside as well as a 300x7 mm BA-X8 (7-10 μ) anion exchange column at 80 °C eluted with an aqueous buffer of 0.162 M $(NH_4)_2SO_4$ and 0.038 M $MgSO_4$ at pH 8.

β-cyclodextrin samples were analysed by HPLC on a Waters 625 LC system equipped with a Dionex Carbopac PA1 column in combination with a Dionex PED 1 pulsed electrochemical detector and a Spectra-Physics SP4270 integrator. A Waters pump and controller were used to apply the desired solvent gradient. The solvents used for the mobile phase were: A: 0.1 M aqueous NaOH; B: 0.1 M aqueous NaOH, 0.5 M sodium acetate. Gradient program: t=0 min. 100% A; t=35 min. 50% A, 50% B; t=40 min. 20% A, 80% B; t=45 min. 100% B; t=55 min. 100% A. Times and voltages for the electrochemical cell of the detector: measuring period T_1 0-0.50 s, U_1 0.05 V; oxidation period T_2 0.51-0.60 s, U_2 0.80 V; reduction period T_3 0.61-0.70 s, U_3 -0.60 V.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-400S spectrometer and on a Nicolet NT-200 WB spectrometer, using D_2O as solvent and *tert*-butyl alcohol as internal reference.

Oxidation of *Trans*-1,2-cyclohexanediol was performed in 100 mL aqueous solutions of 1.5 and 0.5M KOH (pH of 14.2 and 13.7 respectively). Both hydroxide concentrations were equally effective. 1.5 g (13 mmol) of *trans*-1,2-cyclohexanediol was dissolved; 0.5 g catalyst was added and after flushing with oxygen the autoclave was pressurised to 15-20 bar of O_2 and the temperature was brought to the desired value in 5-10 minutes. Analysis was carried out by HPLC using commercial samples as references.

Oxidation of Methyl α-D-glucopyranoside. In a typical oxidation 1-2 g (5-10 mmol) of methyl α-D-glucopyranoside was dissolved in 100 mL of water in an autoclave reactor; 4.0 g (71 mmol) of KOH was added and dissolved. 0.5-1.0 g of ruthenium bismuth pyrochlore oxide catalyst was added and after flushing with oxygen the mixture was pressurised to 20 bar of O_2. The temperature was brought to 70 °C in about 10 minutes. The pH of the reaction mixture changed from 13.8 to about 13 at the end of the reaction.

Isolation of the reaction products was performed by preparative anion exchange chromatography. A Pharmacia column of 28x500 mm was packed with 250 mL of Dowex 1X8-200 resin obtained from Janssen Chimica. An eluent flow of 7.5 mL/min was applied using a Masterflex 7523-05 peristaltic pump. Products were detected using a Waters R403 differential refractometer. After eluting the uncharged compounds with water, a solution of 0.25 M $(NH_4)_2CO_3$ was used to carefully elute a series of carboxylates. The $(NH_4)_2CO_3$ was removed by evaporation and the reaction products were identified by NMR as dipotassium (*R*)-3-*O*-[(*R*)-carboxylato-(methoxy)-methyl] (*R*)-2,4-dihydroxybutanoate (**2**), dipotassium (*R*)-2-*O*-[(*R*)-carboxylato-(methoxy)-methyl] 3-hydroxypropanoate (**3**). The products resulting from oxidation at the primary hydroxyl group of C(6) were 1-*O*-methyl α-D-glucuronate and the tripotassium salt of 2-*O*-[(*R*)-carboxylato-(methoxy)-methyl]-propanedioic acid (**4**).

Product **2** was reported[12] by Mombarg et al. The products **2**, **3** and **4** were subsequently identified by ^{1}H NMR. The spectrum of **2** resembles very much that of the oxidation product of methyl 4,6-*O*-isopropylidene-α-D-glucopyranoside reported earlier.[7]

The ^{1}H NMR data for product **3** are in accordance with the results of Nieuwenhuizen et al.,[13] but because TNP (sodium 3-trimethylsilyl-2,2,3,3-tetradeuteropropionate) was used as internal standard, all signals reported here are shifted 0.1-0.2 ppm downfield.

Oxidation of β-cyclodextrin. In a typical oxidation experiment 1.0 g (0.88 mmol) β-cyclodextrin was dissolved in 100 mL of water; 4.0 g (71 mmol) of KOH was

Table 1. ^{13}C NMR of Methyl α-D-Glucopyranoside and Oxidation Products

Compound	OMe	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Me α-D-glucoside	56.3	99.9	72.1	74.1	70.5	72.5	61.6
1-*O*-me-glucuronate	56.7	100.8	72.7	74.5	73.5	73.5	178.1
C2-C3 prod. **2**	55.0	103.0	179.3	176.0	82.5	74.8	62.2
C2-C4 prod. **3**	55.2	102.0	178.7	--	175.2	81.6	63.7
tricarboxylate **4**	54.8	101.0	176.3	--	174.3	81.7	174.8

Table 2. ^{1}H NMR of Dipotassium (*R*)-3-*O*-[(*R*)-Carboxylato-(methoxy)-methyl] (*R*)-2,4-dihydroxybutanoate (**5**)

δ (ppm)	signal	H's	structure	no.	J (H_a,H_b)	J (Hz)
4.89	s	1H	C<u>H</u>OCH$_3$	1		
4.26	d	1H	HC(4)	2	(2,3)	3.3
3.98	dt	1H	HC(5)	3	(3,4), (3,4')	3.3, 7.8
3.73	dd	1H	H_AC(6)	4	(4,4')	12.2
3.57	dd	1H	H_BC(6)	4'		
3.35	s	3H	OCH$_3$	5		

Table 3. ^{1}H NMR of Dipotassium (*R*)-3-*O*-[(*R*)-Carboxylato-(methoxy)-methyl] 3-hydroxypropanoate (**3**)

δ (ppm)	signal	H's	structure	no.	J (H_a,H_b)	J (Hz)
4.84	s	1H	C<u>H</u>OCH$_3$	1		
4.08	dd	1H	HC(5)	2	(2,3), (2,3')	3.1, 5.4
3.81	dd	1H	H_AC(6)	3	(3,3')	12.2
3.73	dd	1H	H_BC(6)	3'		
3.31	s	3H	OCH$_3$	4		

Table 4. ^{1}H NMR of Tripotassium Salt of 2-*O*-[(*R*)-Carboxylato-(methoxy)-methyl]-propanedioic acid (**4**)

δ (ppm)	signal	H's	structure
4.74	s	1H	C<u>H</u>OCH$_3$
4.38	s	1H	HC(5)
3.27	s	3H	OCH$_3$

Table 5. Typical Retention Times of β-Cyclodextrin and Main Products

Product	Pr1	Pr2	Pr3	Pr4	β-CD	Pr5	Pr6
Ret. time	19.0	22.2	25.2	27.7	32.0	34.9	41.4

added. 1.0 g of RuBi (9,6,3) or RuBi (9,6,3)/C catalyst was added and after flushing with oxygen the autoclave was pressurised to 20 bar of O_2. The temperature was brought to 70 °C in about 10 minutes.

For desalination, a laboratory ultrafiltration apparatus was constructed suitable for filtration of 180 mL liquid at a nitrogen pressure of 25 bar. The salt was removed from the reaction mixtures at pH 7 using a UTC-60 membrane from Toray Industries, Japan (separation limit: molecular weight of about 500, depending on the pressure applied).

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