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Hydrogenation of gluconolactones in equilibrium with gluconic acid on ruthenium catalyst

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Water solutions of glucono-δ-lactone and glucono-γ-lactone in equilibrium with gluconic acid were hydrogenated with molecular hydrogen in the presence of a commercial carbon-supported ruthenium catalyst (5% Ru/C, Engelhard Escat 40). Reactions were conducted batchwise on 20 wt% solutions under 100 bar pressure in the temperature range 80–140 °C. Reaction rates were unexpectedly high at moderate temperatures (e.g., 0.58 $\mathrm{mol\,h^{-1}\,g_{Ru}^{-1}}$ at 100 °C) because lactones were probably the reactive species. The selectivity to sorbitol at total conversion was larger than 99% at temperatures lower than 100 °C. Kinetic study was done at different temperatures, pressures and concentrations. Modelling of the reaction kinetics showed that the reaction followed a rate law corresponding either to the Langmuir–Hinshelwood mechanism without H_2 dissociation, or to the Horiuti–Polanyi mechanism.

Keywords: ruthenium catalyst, gluconic acid, gluconolactones, carbohydrate hydrogenation, sorbitol

1. Introduction

The development of processes for the production of chemicals from renewable resources is a major challenge for the forthcoming decades. Carbohydrate molecules such as glucose extracted from polysaccharide-containing crops can be used as cheap building blocks for chemistry. The transformation of carbohydrates into useful products is best achieved by using clean and selective catalytic processes; particularly, it is desirable to develop processes based on heterogeneous catalysts that can be easily separated from the reaction medium. Heterogeneous catalysts are well suited to perform hydrogenation and oxidation reactions on carbohydrates. Thus, the hydrogenation of aldoses and ketoses on metal catalysts to produce polyols is a well-known industrial process carried out on a large scale. A recent study [1] showed that glucose hydrogenation can be performed continuously in a trickle-bed reactor over ruthenium catalysts, with a selectivity to sorbitol higher than 99% at total conversion. Heterogeneous catalysts based on carbon-supported palladium–bismuth catalysts have been also used with success to oxidize aldoses into aldonic acids with selectivity to sorbitol higher than 98% at total conversion [2,3].

The present work was aimed at studying other metal-catalyzed processes of general application for the conversion of carbohydrates, more specifically, the conversion of aldonic acids and their lactones into polyols. This reduction can be achieved with the sodium amalgam [4] or with metal hydrides [5], but, to our knowledge, metal-catalyzed hydrogenations were not extensively studied. Glucono-δ-lactone **2** and glucono-γ-lactone **3** in equilibrium with gluconic acid **1**, were hydrogenated to sorbitol **5** through the transient formation of glucose **4** (figure 1). Ruthenium catalysts were selected for their ability to hydrogenate carboxylic acids and lactones [6].

2. Experimental

Glucono-δ-lactone in pure crystallized form was provided by Roquette Frères. The 5 wt% Ru/C catalyst in powder form was obtained from Engelhard (Escat 40). The metal dispersion on the support was measured by high-resolution electron microscopy (Jeol Jem 2000).

Reactions were conducted in a 150 ml autoclave lined with graphitized Teflon to avoid corrosion in acidic and chelating medium. The autoclave was stirred with a Rushton-type turbine in graphitized Teflon mechanically driven at 1600 rpm. The autoclave was equipped with all the necessary inlets (argon and hydrogen lines, dropping funnel for liquid) and outlets (gas exhaust, safety head, liquid sampling tube). The standard procedure for hydrogenation reactions involved the following steps. The dropping funnel was loaded with 33 g of a 50 wt% solution of glucono-δ-lactone, which was maintained at 40 °C to avoid crystallization. The autoclave was loaded with 0.6 g of 5 wt% Ru/C catalyst suspended in 50 ml of water, purged with argon, pressurized under 60 bar of hydrogen, and heated to 140 °C under continuous stirring overnight in order to standardize the reduction state of the catalyst before use. The dropping funnel and autoclave were heated to the reaction temperature (140 °C), hydrogen pressure was equilibrated at 100 bar in these vessels, then the solution

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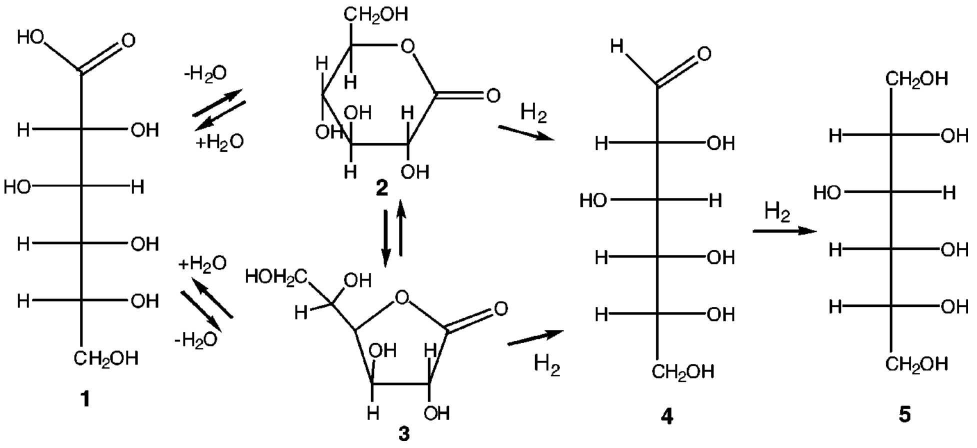

Figure 1. Simplified formal reaction scheme. **1** – gluconic acid, **2** – glucono-δ-lactone, **3** – glucono-γ-lactone, **4** – glucose and **5** – sorbitol.

was dropped in the autoclave which marked time zero of the reaction. Samples of the reaction medium were taken at various time intervals to follow the conversion and product distribution. Solutions were analysed by GC after derivatization by silylation with a mixture of trimethylchlorosilane and hexamethyldisilazane in pyridine. Products were separated with a DB1 column and detected with a Shimadzu GC14B chromatograph with FID detector. The C_6 polyols were also analysed by HPLC (HPX87C column at 85 °C, eluent water, RID detector).

3. Results and discussion

3.1. Preliminary experiments

The equilibrium between gluconic acid and its lactones was studied at different temperatures under conditions similar to those used during hydrogenation experiments. The solution obtained by dissolving 20 wt% of pure cristallized glucono-δ-lactone in water was pressurized under 50 bar of argon, and stirred in an autoclave at temperatures between 30 and 148 °C. The concentrations of chemical species present in solution at a given temperature were determined by GC analysis of liquid samples. The relative molar fractions of the compounds present in the solutions after attaining the equilibrium are given in figure 2. Whatever the temperature, glucono-δ-lactone was in equilibrium with glucono-γ-lactone and gluconic acid. It was verified that the composition at equilibrium did not depend upon the initial concentration in glucono-δ-lactone in the range 5–40 wt% at 148 °C. The period of time necessary to reach the equilibrium was 5 min at 148 °C, but the rate of interconversion was much smaller at lower temperatures.

To verify that the hydrogenation reaction was performed in the absence of gas–liquid and liquid–solid mass transfer, experiments were conducted at 140 °C and 100 bar of H_2 at different stirring speeds and with different masses of catalyst. The initial rate of reaction did not depend upon the stirring speed above ca. 300 rpm. All the subsequent experiments were conducted at 1600 rpm. The specific rate of reaction remained constant whatever the mass of catalyst in the range 0–4 g. Therefore, under standard conditions (0.6 g of catalyst, 1600 rpm), the reaction kinetics was not limited by external mass transfers. These tests did not rule out the possibility of internal mass transfer limitation due to internal diffusion in catalyst pores. It was not possible to test the influence of catalyst particle size because grinding the fine catalyst powder was not feasible. However, calculation of Thiele-type modulus [7] showed that the effectiveness factor was one which indicated that intraparticle diffusion was not rate limiting.

The BET surface of the commercial 5.1 wt% Ru/C catalyst was 900 $m^2\,g^{-1}$. TEM examination of the fresh catalyst indicated that most of the metal particles were in the size range 1–4 nm, with an mean size of 2 ± 0.5 nm. They were uniformly distributed on the carbon support. No changes in metal dispersion and distribution were detected by TEM examination of the catalyst after reaction. Analysis of the reaction medium by ICP-AES showed that ruthenium did not leach within the accuracy limit of 0.05 ppm.

3.2. Reaction selectivity

Figure 3 gives the distribution of reactants and products as a function of time during the hydrogenation of 20 wt% glucono-δ-lactone water solution under standard conditions in the presence of the 5% Ru/C catalyst. The three reactant molecules (gluconic acid, glucono-δ-lactone, and glucono-γ-lactone) were present at time zero and disappeared as a function of time in such a way that their molar ratio remained constant. This does not mean that they were hydrogenated at the same rate, but that the mutual interconversion of the three reactants was faster than the rate of hydrogenation. This point was confirmed by carrying hydrogenation experiments at 60 °C, temperature at which the period of time to reach the equilibrium was very long; the lactones were hydrogenated slowly while the concentration of gluconic acid remained constant, which means that lactones were the reactive species. This is in agreement with previous reports showing that esters and lactones are hydrogenated more easily than carboxylic acids [6]. At

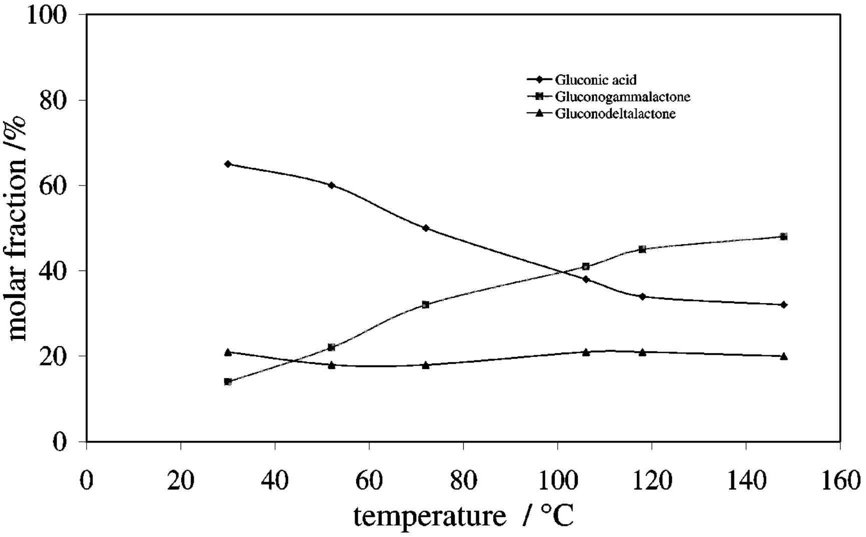

Figure 2. Relative molar fraction of gluconic acid, glucono-δ-lactone and glucono-γ-lactone in aqueous solution (20 wt% dry matter) measured at equilibrium under argon as a function of temperature.

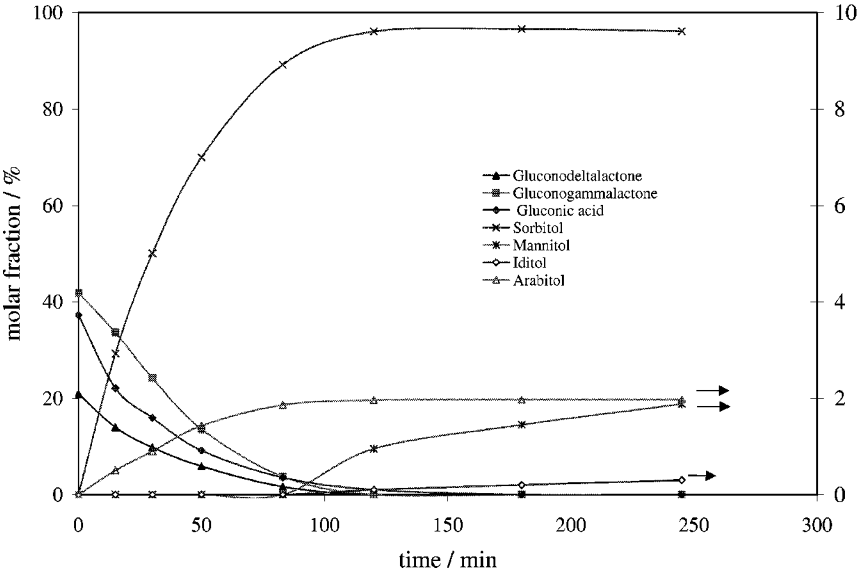

Figure 3. Distribution of reactants and products as a function of time during hydrogenation of 20 wt% solution of acid and lactones (0.6 g of 5% Ru/C catalyst, 140 °C, 100 bar H_2 pressure).

140 °C, the selectivity to sorbitol at 100% conversion was 96%, arabitol being the main primary by-product formed by decarboxylation. After total conversion the amount of sorbitol present in the reaction medium started to decrease because of its isomerization into other C_6 polyols, mainly mannitol and traces of iditol. The selectivity to sorbitol increased at lower reaction temperatures and reached 99% at temperatures lower than 100 °C. At these temperatures the transient formation of glucose was observed, thus at 100 °C, a maximum 4% yield in glucose was measured at 20% lactone conversion.

3.3. Reaction kinetics and modelling

The specific hydrogenation rate at 140 °C and 100 bar H_2 pressure was 2.7 $\mathrm{mol\,h^{-1}\,g_{Ru}^{-1}}$. Taking into account TEM measurements pointing to an average particle size of 2 nm, the corresponding turnover frequency was ca. 400 $\mathrm{h^{-1}}$.

The reaction was conducted under different temperatures, hydrogen pressures and initial concentrations of glucono-δ-lactone. The activation energy deduced from the slope of the Arrhenius transform, obtained by measuring the initial reaction rate between 80 and 140 °C, was 50 $\mathrm{kJ\,mol^{-1}}$. Figure 4(a) gives the data points of the initial rate of reaction as a function of the hydrogen pressure. The reaction followed a first-order-rate law with respect to pressure ($r = 0.026\ P_{H_2}$ with r expressed in $\mathrm{mol\,h^{-1}\,g_{Ru}^{-1}}$, and P_{H_2} in bar). Measurements of the reaction rate with respect to the initial concentration of reactant (figure 4(b)) showed that the rate followed a first-order dependency with the concentration at concentrations smaller than 1 $\mathrm{mol\,l^{-1}}$,

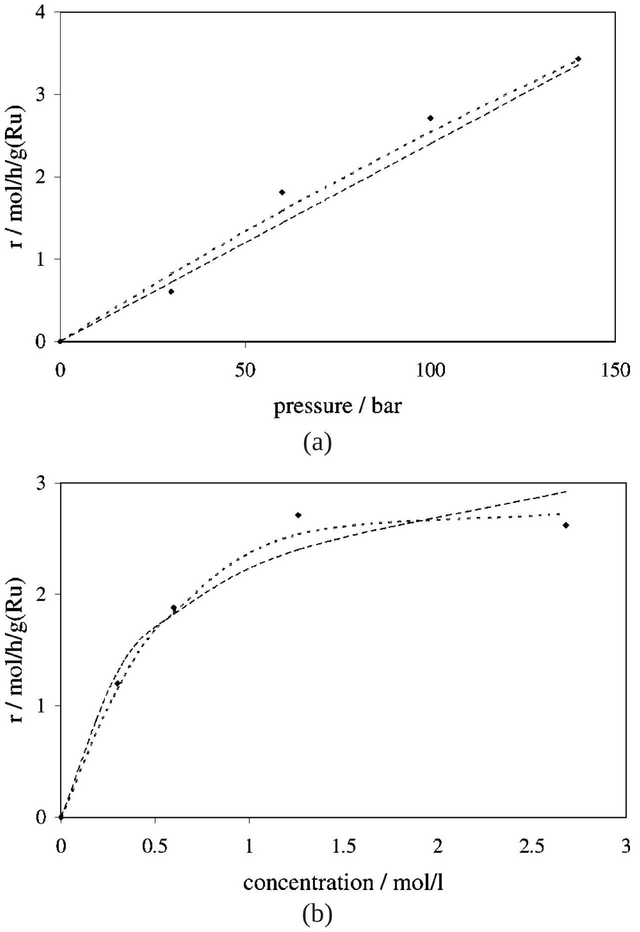

Figure 4. Comparison between the experimental reaction rates (0.6 g of catalyst, 140 °C) and the rates calculated from equations (1) and (3). (◆) Data points, (- - -) rate equation (3), (· · ·) rate equation (1). (a) Rate vs. H_2 pressure (20 wt% solution) and (b) rate vs. initial reactant concentration (100 bar H_2 pressure).

then at higher concentrations, a zero order was observed. It was verified that the addition of sorbitol to the initial reaction medium did not change the rate of hydrogenation.

It was attempted to model the reaction kinetics taking into account the fact that the lactones were hydrogenated into glucose, detected transiently at low temperatures, which was then hydrogenated very fast into sorbitol. The rate equations have been established for different hydrogenation mechanisms, namely:

(1) Langmuir–Hinshelwood with hydrogen molecularly adsorbed on the metal surface;

(2) Langmuir–Hinshelwood with hydrogen dissociatively adsorbed, addition of the first hydrogen rate limiting;

(3) Horiuti–Polanyi with hydrogen dissociatively adsorbed, addition of the second hydrogen rate limiting;

(4) Eley–Rideal involving molecular hydrogen, not or weakly adsorbed.

The rate constants and adsorption coefficients were determined from the linear transform of the rates using the flexible simplex method [8]. The following rate equations were obtained:

$$r = \frac{0.0555[\text{lactone}]_0 P_{\mathrm{H_2}}}{(1 + 0.49[\text{lactone}]_0 + 0.0008 P_{\mathrm{H_2}})^2}, \tag{1}$$

$$r = \frac{8.49[\text{lactone}]_0 P_{\mathrm{H_2}}^{1/2}}{(1 + 0.49[\text{lactone}]_0 + 0.0064 P_{\mathrm{H_2}}^{1/2})^2}, \tag{2}$$

$$r = 0.0524 P_{\mathrm{H_2}} \times \frac{1 + 3.57[\text{lactone}]_0 - (1 + 7.50[\text{lactone}]_0)^{1/2}}{7.50[\text{lactone}]_0}, \tag{3}$$

$$r = \frac{0.0065[\text{lactone}]_0 P_{\mathrm{H_2}}}{1 + 1.91[\text{lactone}]_0}. \tag{4}$$

The best agreement between the experimental data points and the rate equations was obtained for mechanisms (1) and (3), as shown in figure 4 (a) and (b), corresponding to the dependency of the reaction rate on hydrogen pressure and reactant concentration, respectively.

4. Conclusion

This study shows that the total hydrogenation of the two gluconolactones in equilibrium with gluconic acid can be achieved on ruthenium catalysts at comparatively low temperatures. Thus, the reaction rate at 100 °C was as high as 0.58 $\mathrm{mol\,h^{-1}\,g_{Ru}^{-1}}$ and the selectivity to sorbitol at temperatures lower than 100 °C was at least 99%. These interesting activity and selectivity data were rather unexpected from literature data suggesting that higher temperature and pressure conditions would be needed. Since the present data were obtained with a commercial catalyst, which was not specifically designed for this particular reaction, one can even expect better results with optimized catalysts, e.g., with ruthenium promoted by other metals. The activity and selectivity obtained with this model reaction are encouraging enough to envisage the extension of this ruthenium-catalyzed hydrogenation method to other lactones and acids of interest in carbohydrate chemistry.

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