

# Catalytic Hydrogenation of Arabinonic Acid and Lactones to Arabitol

Lionel Fabre, Pierre Gallezot,<sup>1</sup> and Alain Perrard*Institut de Recherches sur la Catalyse-CNRS, 2, avenue Albert Einstein, 69626 Villeurbanne Cédex, France*

Received December 11, 2001; revised February 4, 2002; accepted February 8, 2002

Aqueous solutions (20 wt%) of arabinonic acid in equilibrium with arabinonolactones were hydrogenated on ruthenium catalysts at 100°C or lower temperatures in a batch reactor. The highest selectivity to arabitol was 98.9% at 98% conversion, with a reaction rate of 73 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup> at 80°C. Reaction modeling was achieved by a detailed kinetic analysis of reaction data under various reaction conditions. The conversion of substrate follows a rate equation established with the Horiuti–Polanyi mechanism. The selectivity was higher on small particles supported on carbon supports because of an electron-donating effect of the support on the ruthenium particles, which decreases the rate of dehydroxylation reactions leading to unwanted deoxy products. The most important factor enhancing the selectivity was the presence of anthraquinone-2-sulfonate (A2S), which decreased the formation of deoxy products. With an optimum amount of A2S the selectivity at 100°C was improved from 93.6 to 96.7%. The molecule acted as a permanent surface modifier since the catalyst was recycled with the same selectivity without further addition of A2S. The molecule could act as an electron-donating surface ligand decreasing the rate of dehydroxylation reactions. © 2002 Elsevier Science (USA)

## 1. INTRODUCTION

In a previous work (1) we showed that active carbon-supported ruthenium catalysts were highly effective at hydrogenating water solutions of gluconic acid in equilibrium with  $\gamma$ - and  $\delta$ -gluconolactones to obtain 99% yield in sorbitol at temperatures lower than 100°C. Although this reaction presents no practical interest it serves as a model for the reduction of other aldonic acids and aldonolactones to more valuable polyols. Indeed there is a great interest in converting C<sub>6</sub> carbohydrates into C<sub>5</sub> polyols used as food or care product additives. Thus, glucose available in large supply from renewable resources can be converted via a two-step process to arabitol. The first step is an oxidative decarboxylation of glucose into arabinonic acid in the presence of soluble basic catalysts. Arabinonic acid **1** in aqueous solutions is in equilibrium with the corresponding  $\gamma$ -lactone **2** and  $\delta$ -lactone **3** (Fig. 1). The second step is the catalytic hydrogenation of arabinonic acid and lactones to obtain

arabitol **4**. The selectivity of the hydrogenation step can be impaired by decarboxylation and epimerization reactions leading to other sugar polyols, but the main problem is to avoid dehydroxylation reactions leading to deoxy products not compatible with the purity specifications required for arabitol (Fig. 1). The hydrogenation of arabinonic acid has been described in the patent literature (2, 3), but, to our knowledge, there have been no studies on the kinetics of this reaction or on the factors affecting its selectivity. We published recently a short account of preliminary work (4). The present work is an in-depth study of the catalytic hydrogenation of arabinonic acid in equilibrium with its lactones, aimed at determining the best catalysts and reaction conditions for obtaining the highest selectivity to arabitol. Commercial ruthenium catalysts as well as various, laboratory-prepared, ruthenium catalysts were tested with different lots of arabinonic acid solutions.

## 2. EXPERIMENTAL

### 2.1. Starting Materials

Aqueous solutions containing about 50 wt% of arabinonic acid in equilibrium with  $\gamma$ - and  $\delta$ -lactones were provided by Roquette Frères. Different lots of solutions containing variable amounts of impurities formed in the oxidative decarboxylation of glucose were tested after having been diluted at 20 wt%. Their composition is given in Table 1.

### 2.2. Catalysts

Most of the kinetic studies were performed on two similar 5 wt% Ru/C catalysts in powder form obtained from Engelhard (ESCAT 40 and 9000). Other commercial catalysts with different metals were tested for comparison (Table 2).

A ruthenium catalyst (4.8% Ru/C–Norit) was prepared by cationic exchange of an active carbon (Norit SX Ultra) with [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ions in basic medium and reduction in flowing H<sub>2</sub> at 300°C, as described in previous work (5). Measurements by high-resolution electron microscopy (JEOL Jem2000) indicated the presence of 1- to 2-nm Ru particles homogeneously distributed on the support. Using the same preparation technique the 2.5% Ru/C–Norit sample was

<sup>1</sup> To whom correspondence should be addressed. E-mail: [gallezot@catalyse.univ-lyon1.fr](mailto:gallezot@catalyse.univ-lyon1.fr).

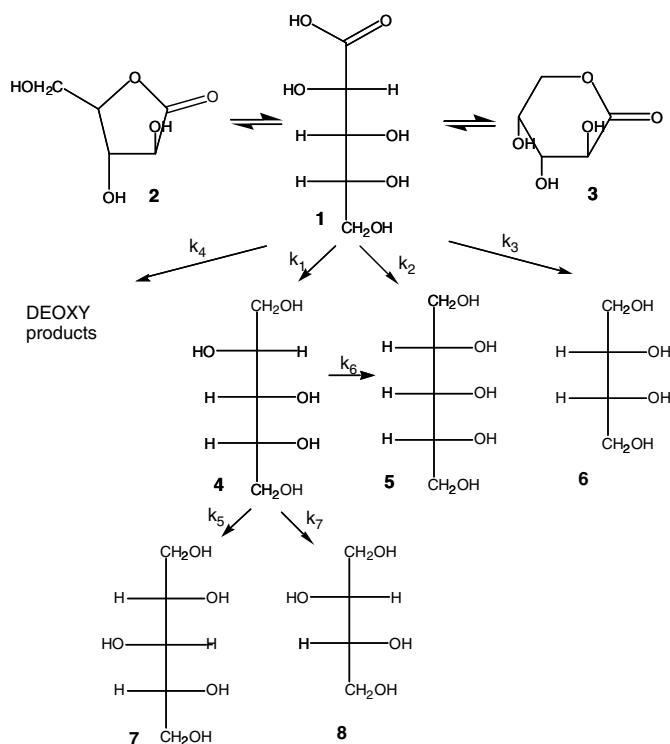


FIG. 1. Hydrogenation of arabinonic acid and lactones. Simplified reaction scheme. **1**, arabinonic acid; **2**,  $\gamma$ -lactone; **3**,  $\delta$ -lactone; **4**, arabitol; **5**, ribitol; **6**, erythritol; **7**, xylitol; and **8**, threitol.

obtained with a similar metal dispersion. The 1- to 2-nm particles of this sample were grown bigger by deposition of ruthenium metal from acidic  $\text{RuCl}_3$  solutions with an oxido-reduction process involving hydrogen atoms adsorbed on a metal surface, as described for Pt particles in a previous work (6). The resulting 5.4% Ru/C–Norit catalyst exhibited 3- to 5-nm Ru particles uniformly distributed on the support. The different catalysts employed in this study are listed in Table 2.

### 2.3. Reactions Studies

Reactions were conducted in a 150-ml autoclave lined with graphitized Teflon to avoid corrosion in the acidic

TABLE 1  
Composition of Solutions

	Substrate (wt%)			
	AR0 <sup>a</sup>	AR1 <sup>a</sup>	AR4 <sup>a</sup>	AR5
Arabinolactones	31.5	36.6	38.9	34.5
Arabinonic acid	11.5	11.7	16.2	13.2
Anthraquinone-2 sulfonate	0	Traces <sup>b</sup>	0	0

<sup>a</sup> Solutions containing low amounts of other carboxylic, mainly oxalic, acids ( $\Sigma c < 1.5$  wt%).

<sup>b</sup> Detected by UV absorption spectroscopy (330 nm) but not quantified.

TABLE 2

Characteristics of Catalyst Samples

Catalyst	Origin/preparation	Particle size (nm)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
5% Pt/C	Engelhard (ESCAT 21)		850
5% Pd/C	Engelhard (ESCAT 11)		950
3.6% Rh/C	Aldrich		
5.1% Ru/C	Engelhard (ESCAT 40 or 9000)	3–6	850
2.8% Ru/TiO <sub>2</sub>	Engelhard	4–5	50
4.8% Ru/C–Norit	Cationic exchange of oxidized Norit-active carbon with $\text{Ru}(\text{NH}_3)_6^{3+}$	1–2	1250
2.5% Ru/C–Norit	Cationic exchange of oxidized Norit-active carbon with $\text{Ru}(\text{NH}_3)_6^{3+}$	1–2	1250
5.4% Ru/C–Norit	Electronless Ru deposition on 2.5% Ru/C–Norit	3–5	1250
4.2% Ru/HY	Cationic exchange of HY zeolite with $\text{Ru}(\text{NH}_3)_6^{3+}$	<1.2	

and chelating reaction medium. The autoclave was stirred with a Rushton-type turbine in graphitized Teflon mechanically driven at 1600 rpm. The standard procedure for hydrogenation reactions involved the following steps. A dropping funnel connected with the autoclave was loaded with 33 g of the 50 wt% aqueous solution of arabinonic acid and lactones. The autoclave was loaded with 0.6 g of catalyst powder 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, hydrogen pressure was equilibrated at 100 bar in these vessels, then the solution was dropped into 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 analyzed by GC after derivatization by silylation with a mixture of trimethylchlorosilane and N,O-bis(trimethylsilyl)trifluoroacetamide in pyridine. Products were separated with a DB1 column temperature programmed from 80 to 250°C and detected with a Shimadzu GC14B chromatograph with a FID detector. The C<sub>6</sub> polyols were also analyzed by HPLC (HPX87C column at 85°C, water eluent, RID detector).

## 3. RESULTS AND DISCUSSION

### 3.1. Preliminary Studies

*Equilibrium between arabinonic acid and lactones.* The equilibrium between arabinonic acid **1**,  $\gamma$ -lactone **2**, and  $\delta$ -lactone **3** in aqueous solutions of lot AR0 was studied

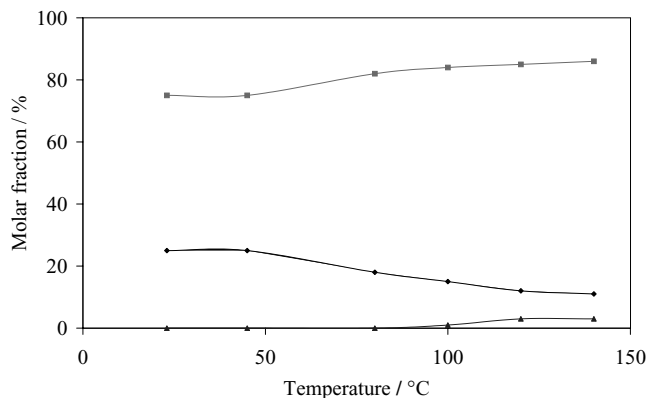


FIG. 2. Equilibrium between arabinonic acid **1**,  $\gamma$ -arabinonolactone **2**, and  $\delta$ -arabinonolactone **3** in water solution as a function of temperature. ♦, **1**; ■, **2**; and ▲, **3**.

at different temperatures. The solutions were pressurized under 50 bar of argon in an autoclave and stirred at temperatures between 20 and 140°C. The concentration of dissolved species at a given temperature was determined by GC analysis of liquid samples taken from the solution at equilibrium. The relative molar fractions are given in Fig. 2. The  $\gamma$ -lactone was always in equilibrium with arabinonic acid, but its concentration increased slightly with temperature while the  $\delta$ -lactone appeared at temperatures higher than 80°C. It was verified that the equilibrium composition at 20 and 100°C did not depend upon the initial concentration of substrate in solution in the range 10–50 wt%. From the values of the equilibrium constants at different temperatures, the enthalpies of dehydration of arabinonic acid to  $\gamma$ - and  $\delta$ -lactones determined with the Van't Hoff law were 11 and 45 kJ mol<sup>-1</sup>, respectively.

**Stability of reactants and products.** It was verified that the relative concentrations of the acid and lactones in solutions pressurized under 60 bar of argon were stable with time, whether or not the Ru/C catalyst was present in the stirred solution. In contrast, arabitol, the hydrogenation product, was not stable in solution. Thus, as a pure arabitol solution was maintained for 140 h at 100°C under hydrogen pressure in the presence of the 5.1% Ru/C catalyst, 15.4% of arabitol was epimerized into xylitol (8.5%) and ribitol (5.8%). Only a low fraction was converted to deoxy products (0.3%), which indicates that they are primary reaction products in the hydrogenation of arabinonic acid (vide infra).

**Effect of stirring speed and catalyst mass.** It was verified that under the standard reaction conditions (100°C, 100 bar of H<sub>2</sub>, 0.6 g of catalyst) the reaction rate was independent of the stirring speed above 200 rpm and that the rate of arabitol formation expressed in millimoles per hour increased linearly with the catalyst mass up to 1.2 g (Fig. 3). This indicates that there was no external mass transfer limitation

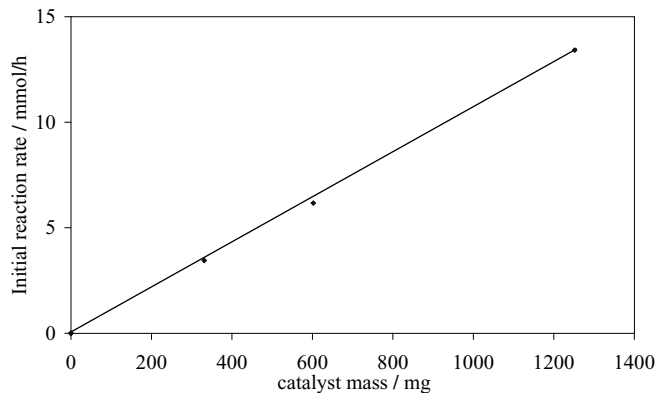


FIG. 3. Initial rate of arabitol formation as a function of catalyst mass.  $T = 100^\circ\text{C}$ ,  $P(\text{H}_2) = 100$  bar, 0.6 g of 5.1% Ru/C, lot AR0.

when the reaction was conducted on the standard mass of 0.6 g of catalyst.

### 3.2. Influence of Reaction Conditions on Selectivity

The product distribution obtained after hydrogenation of arabinonic acid solution (lot AR0, Table 1) at different temperatures is given in Table 3. The best selectivity was obtained at 80°C; increasing the temperature enhanced the C–OH bond rupture (formation of deoxy products), the C–C bond rupture (formation of erythritol **6**), and the epimerization of arabitol into xylitol **7** and ribitol **5**. However, because of the lower reaction rate at 80°C, the standard reaction temperature was set at 100°C.

The influence of the pH on selectivity and activity was studied by conducting the reaction at pH 2.5, which is the normal pH of a 20 wt% solution of arabinonic acid and lactones, and at pH 5, obtained by partial neutralization of the solution with sodium hydroxide. Table 4 indicates that both the rate and selectivity decreased at pH 5. The lower rate can be attributed to the smaller adsorption coefficient of arabinonate ions on the metal compared to arabinonic acid. The lower selectivity is due to the epimerization of arabitol into ribitol (Table 4). At higher pH the rate and selectivity decreased further, whereas at pH lower than 2.5

TABLE 3

Product Distribution as a Function of Temperature<sup>a</sup>

Temperature (°C)	Arabitol	Xylitol	Ribitol	Erythritol	Threitol	Deoxy products
80	95.7%	0.2%	0.6%	1.2%	0.1%	2.2%
100	94.0%	0.5%	0.7%	1.4%	0.1%	3.3%
120	94.9%	1.0%	2.3%	1.7%	nd	nd
140	90%	1.7%	2.8%	4.3%	nd	nd

<sup>a</sup> At 98% conversion,  $P(\text{H}_2) = 100$  bar,  $M_{\text{catalyst}} = 0.6$  g (5.1% Ru/C), substrate AR0.

TABLE 4  
Effect of pH on Reaction Rate and Product Distribution

pH	Initial rate (mmol h <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Conversion (%)	Arabitol (%)	Xylitol (%)	Ribitol (%)	Erythritol (%)	Deoxy products (%)
2.5	227	98	94.5	0.4	0.8	0.6	3.5
5	128	94	88.5	0.1	4.0	—	3.5

Note. P(H<sub>2</sub>) = 100 bar, M<sub>catalyst</sub> = 0.6 g (5.1% Ru/C), substrate AR0.

(obtained by adding hydrochloric acid in the reaction medium) no changes of activity and selectivity were observed. The subsequent hydrogenation reactions were all carried without pH control. As conversion proceeded the pH increased from 2.5 to 4, which is the normal pH of a 20 wt% aqueous solution of arabitol.

The reaction data given in Tables 5 and 6 indicate that hydrogen pressure and initial concentration of the organic substrate did not have any significant effect on the selectivity of the reaction.

### 3.3. Kinetics of Arabinonic Acid and Lactones Hydrogenation

*Rate equation for arabitol formation.* From the measurements of the initial rate of arabitol formation in the temperature range 80–140°C, the Arrhenius transform given in Fig. 4 allowed calculation of an activation energy of 49 kJ mol<sup>-1</sup>.

The initial reaction rate of arabitol formation was measured as a function of hydrogen pressure in the 30- to 150-bar H<sub>2</sub>-pressure range (Fig. 5). The linear plot indicates a first-order dependency with H<sub>2</sub> pressure corresponding to the rate law  $r = k P(\text{H}_2)$ , where  $k = 1.43 \times 10^{-3}$  mol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup> bar<sup>-1</sup> at 100°C.

The initial reaction rate was also measured as a function of the substrate concentration (arabinonic acid + lactones). The reaction order was 1 for the domain of concentrations lower than ca. 1 mol L<sup>-1</sup>, then it tended rapidly to 0 above this value (Fig. 6).

The kinetic data of arabinonic acid hydrogenation were similar to those obtained in the hydrogenation of gluconic

TABLE 5  
Effect of Pressure on Product Distribution

Pressure (bar)	Arabitol (%)	Erythritol (%)	Xylitol (%)	Ribitol (%)
80	96.3	1.4	0.7	1.6
100	96.9	1.4	0.4	1.3
130	96.7	1.4	0.7	1.2
150	96.7	1.4	0.7	1.2

Note. T = 100°C, M<sub>catalyst</sub> = 0.6 g (5.1% Ru/C), substrate AR0; threitol and deoxy products not determined.

TABLE 6

Effect of Substrate Concentration on Product Distribution

Concentration (wt%)	Arabitol (%)	Erythritol (%)	Xylitol (%)	Ribitol (%)
10	96.9	1.4	0.4	1.3
20	96.9	1.4	0.4	1.3
40	96.7	1.4	0.5	1.4

Note. T = 100°C, P(H<sub>2</sub>) = 100 bar, M<sub>catalyst</sub> = 0.6 g (5% Ru/C), substrate AR0; threitol and deoxy products not determined.

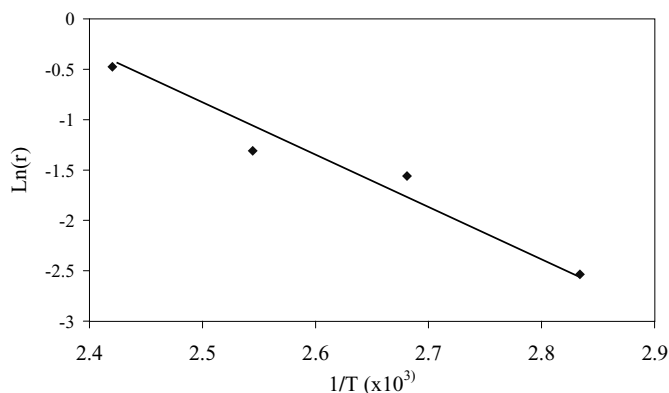


FIG. 4. Arrhenius transform  $\text{Ln}(r_i) = f(1/T)$  with  $r$  in mol per hour per gram of Ru.

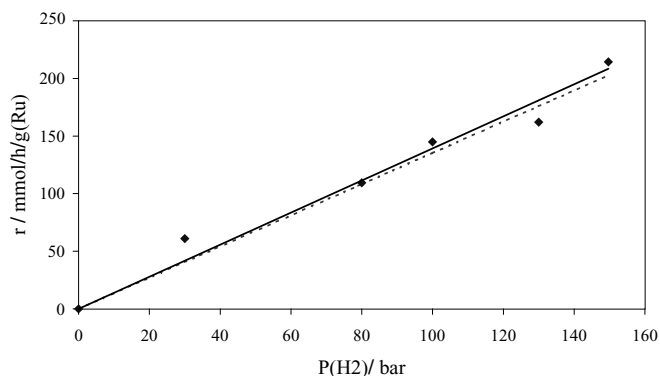


FIG. 5. Initial rate of arabitol formation as a function of hydrogen pressure ( $T = 100^\circ\text{C}$ , 0.6 g of 5.1% Ru/C, lot AR0). Comparison with rate equation calculated by kinetic modeling with Horiuty–Polanyi mechanism (dotted line).

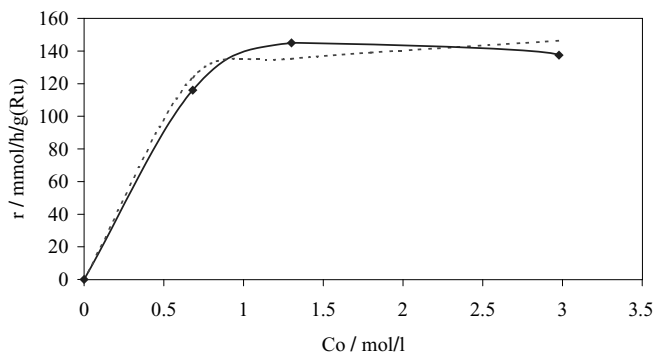


FIG. 6. Initial rate of arabitol formation as a function of initial reactant concentration [1 + 2 + 3]. ( $T = 100^{\circ}\text{C}$ ,  $P(\text{H}_2) = 100$  bar, 0.6 g of 5.1% Ru/C, lot AR0.) Comparison with rate equation calculated by kinetic modeling with Horiuti–Polanyi mechanism (dotted line).

acid (1), except that under similar conditions ( $100^{\circ}\text{C}$ , 100 bar, 0.6 g of 5.1% Ru/C) the rate of formation of arabitol ( $0.2 \text{ mol h}^{-1} \text{ g}_{\text{Ru}}^{-1}$ ) was lower than that of sorbitol ( $0.58 \text{ mol h}^{-1} \text{ g}_{\text{Ru}}^{-1}$ ). An attempt was made to determine a rate equation fitting the experimental data points at  $100^{\circ}\text{C}$ . Modeling of the kinetic of arabitol formation was achieved from the experimental data using the flexible simplex optimization method. The rate equation as a function of hydrogen pressure  $P(\text{H}_2)$  and reactant concentration  $C_0$  obtained with the Horiuti–Polanyi mechanism involving rate-limiting addition of the second reads

$$r = 3.4 \left\{ \left[ (1 + 28.3 C_0) - (1 + 56.5 C_0)^{1/2} \right] / 56.5 C_0 \right\} P(\text{H}_2),$$

with  $r$  in millimoles per hour per gram of Ru,  $C_0$  in moles per liter, and  $P(\text{H}_2)$  in bar.

This equation gives a good agreement with the experimental data, as shown in Figs. 5 and 6.

**Kinetic modeling of product formation.** Figures 7a and 7b give the conversion of reactants (lot AR0, Table 1) and product distribution as a function of time in the standard reaction conditions. Four products were formed initially: arabitol (Fig. 7a), erythritol, ribitol, and deoxy products (Fig. 7b). Xylitol and threitol appeared only after ca. 60% conversion, which indicates that they are secondary reaction products. Ribitol was formed initially but its amount increased after complete conversion of arabinonic acid/lactones, which indicates that it was also formed by an epimerization reaction from arabitol. These results were corroborated by the study of arabitol conversion under reaction conditions (Section 3.1). Taking into account these observations the reaction scheme given in Fig. 1 can be proposed. The rate constants  $k_1, k_2, \dots, k_7$  of the individual reactions were determined from the rates of product formation determined in the experiments of arabinonic hydrogenation and arabitol conversion. The rate constants on a relative scale with respect to arabitol formation ( $k_1 = 1000$ )

are as follows:  $k_2 = 2$ ,  $k_3 = 8$ ,  $k_4 = 42$ ,  $k_5 = 6$ ,  $k_6 = 4$ , and  $k_7 = 0.3$ . The rate of formation of deoxy products ( $k_4 = 42$ ) is by far the highest.

**Determination of the reactive species.** During the hydrogenation of arabinonic acid and lactones at  $100^{\circ}\text{C}$  the molar ratios  $\gamma$ -lactone/ $\delta$ -lactone and lactones/acid remained constant (Fig. 7a), as if the rate of hydrogenation of the different species was similar. However, the hydrogenation rates of the lactones are probably much higher than that of arabinonic acid since it is known from the literature that esters or lactones are easier to reduce than carboxylic acids. The conversion is apparently similar because the rate of the thermodynamic equilibration is higher than the rate of hydrogenation. In an attempt to determine which species were reduced preferentially, the reaction was run at  $60^{\circ}\text{C}$ , a temperature at which the rate of equilibration should be smaller. The concentration of arabinonic acid did not decrease appreciably during the first 200 min whereas lactones were converted ( $33 \text{ mmol h}^{-1} \text{ g}_{\text{Ru}}^{-1}$ ), which would indicate that the lactones are indeed the reactive species, as expected.

### 3.4. Effect of the Nature of Metal

The results given in Table 7 indicate that palladium and platinum were totally inactive for the reduction of

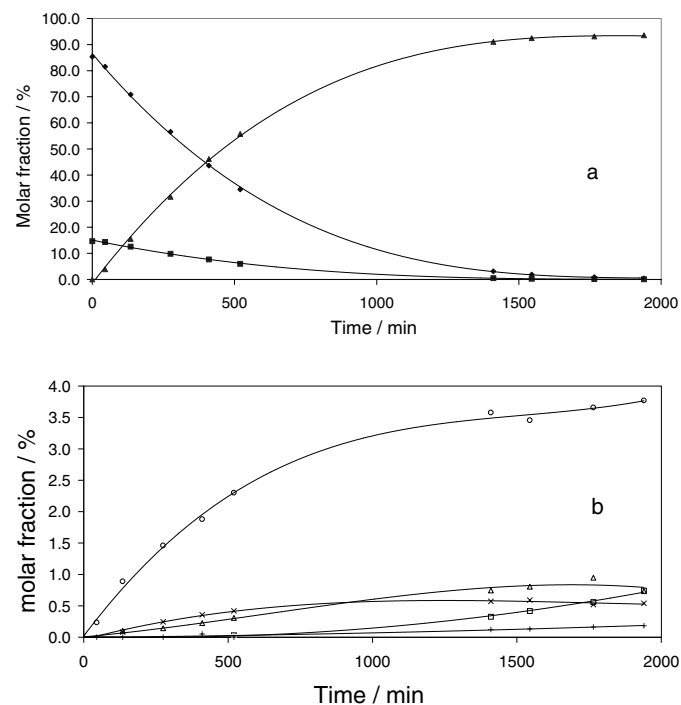


FIG. 7. Hydrogenation of arabinonic acid and arabinonolactones: product distribution vs. time. Sample AR0;  $T = 100^{\circ}\text{C}$ ;  $P(\text{H}_2) = 100$  bar; 0.6 g of 5.1% Ru/C. (a) ■, Arabinonic acid; ◆, lactones (2 + 3); and ▲, arabitol. (b) ○, Deoxy products; △, ribitol; ×, erythritol; +, threitol; and □, xylitol.

TABLE 7  
Initial Activity and Selectivity at 98% Conversion  
on Various Catalysts

Catalyst	Particle size (nm)	Initial rate (mmol h <sup>-1</sup> g <sub>M</sub> <sup>-1</sup> )	Selectivity (%)					
			4	Deoxy	5	6	7	8
5% Pt/C		0						
5% Pd/C		0						
3.6% Rh/C		6.5 <sup>a</sup>	77.0 <sup>a</sup>	18.0 <sup>a</sup>	1.6 <sup>a</sup>	1.5 <sup>a</sup>	0 <sup>a</sup>	1.9 <sup>a</sup>
5.1% Ru/C	3–6	227	94.5	3.5	0.8	0.6	0.4	0.1
2.8% Ru/TiO <sub>2</sub>	4–5	250	94.5	3.7	0.8	0.8	0.3	0.1

Note.  $T = 100^{\circ}\text{C}$ ,  $P(\text{H}_2) = 100$  bar,  $M_{\text{catalyst}} = 0.6$  g, substrate AR0.

<sup>a</sup> 37% conversion.

arabinonic acid and lactones. The rhodium catalyst exhibited some activity but the selectivity was poor because of a high activity compared to dehydroxylated products. All ruthenium catalysts were active, but only carbon and TiO<sub>2</sub> supports were resistant to leaching in the acidic and chelating reaction medium. The activity and selectivity of 5.1% Ru/C and 2.8% Ru/TiO<sub>2</sub> catalysts were very similar on active carbon and TiO<sub>2</sub> supports.

### 3.5. Effects of Metal Particle Size and Support

Table 7 indicates that catalysts 5.1% Ru/C and 2.8% Ru/TiO<sub>2</sub>, which have roughly the same particle size distribution (3–6 nm and 4–5 nm, respectively), have similar activity and selectivity in the hydrogenation of lot AR0. To get a better insight into the effect of particle size two catalysts with quite different particle size distributions were compared in a hydrogenation experiment on another lot of substrate (AR4, Table 1), with every other reaction parameter being similar, including the support since 5.4% Ru/C was obtained from 2.5% Ru/C by electroless surface metal deposition. It is obvious from Table 8 that the smaller particles give a much better selectivity to the desired product **4**. The gain in selectivity was mainly due to the decrease in the formation of deoxy products by the C–OH bond rupture. This could be due to an intrinsic size effect, e.g., the smaller size of surface atom ensembles, or to an electronic effect of the support which should affect mainly very small particles. Indeed it was shown earlier in the case of a carbon-supported platinum catalyst (7, 8) that carbon support acts as an electron-donating ligand on particles in the 1- to 2-nm size range, which would decrease the hydrogenolysis activity of metals. To support this hypothesis, we prepared by ion exchange a Ru/HY catalyst with Ru particles smaller than 1.2 nm. The selectivity to arabitol was very poor (91.7%) because of the formation of deoxy products. This can be interpreted by an electronic support effect, opposite that of carbon; namely, the acidic zeolite support exerts an electron-withdrawing effect on

the small metal particles, thus increasing the hydrogenolysis properties of the metal, as shown in previous studies (7–9).

### 3.6. Effect of Substrate Impurities and Sodium Anthraquinone-2-Sulfonate

Table 9 indicates that the conversion rate of substrate AR5 (460 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>) was two times higher than that of substrate AR0 (227 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>). This was because solution AR5 contained no detectable impurities while carboxylic acids impurities (mainly oxalic acid) with concentrations up to 1.5 wt% were present in solution AR0 (Table 1). These carboxylic acids compete with the arabinonolactones for adsorption on the ruthenium surface, thus decreasing the rate of conversion. The reaction rate is even smaller with substrate AR1 (73 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>), which contains both carboxylic impurities and sodium anthraquinone-2-sulfonate (A2S). Indeed this compound, employed as catalyst in the oxidative decarboxylation of glucose to arabinonic acid, was detected by UV spectroscopy (absorption band at 300 nm) but not quantified. It was verified that by adding increasingly higher amounts of A2S in solution AR5 the reaction rate decreased markedly (Table 9). Clearly A2S added in solution was adsorbed on the metal surface and decreased the rate of arabinonic acid/lactones hydrogenation.

The selectivity data given in Table 9 show that the selectivity to arabitol was greatly increased in solutions containing A2S. Thus, when 2180 ppm of A2S was introduced into A5 solution, the selectivity to arabitol increased from 93.6 to 97.9%. The selectivity gain was mainly due to the decrease from 4.2 to 0.6% in the selectivity to deoxy products. Therefore, A2S adsorbed on ruthenium acts as a modifier of the metal, decreasing the probability for dehydroxylation reactions. This could be attributed to the basic character of A2S, which would act as an electron-donating surface ligand, decreasing the hydrogenolysis properties of the metal. To verify this hypothesis 2000 ppm of triethylamine was added to AR5 solution. The reaction rate measured with the modified solution (AR5-f) decreased, indicating an adsorption of the amine on the metal surface while the

TABLE 8  
Effect of Particle Size on Initial Activity and Selectivity  
at 98% Conversion

Catalyst	Particle size (nm)	Initial rate (mmol h <sup>-1</sup> g <sub>M</sub> <sup>-1</sup> )	Selectivity (%)					
			4	Deoxy	5	6	7	8
2.5% Ru/C–Norit	1–2	198	95.8	2.0	1.3	0.6	0.2	0.1
5.4% Ru/C–Norit	3–5	173	93.9	4.0	1.0	0.7	0.3	0.1
4.2% Ru/HY	<1.2	272	91.7	6.6	0.6	0.6	0.4	0.1

Note.  $T = 100^{\circ}\text{C}$ ,  $P(\text{H}_2) = 100$  bar,  $M_{\text{catalyst}} = 0.6$  g, substrate AR4.

TABLE 9  
Reaction Data in the Presence of Sodium Anthraquinone-2-Sulfonate<sup>a</sup>

Substrate	Amount of A2S <sup>b</sup>	Initial rates (mmol h <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Selectivities at 98% conversion					
			Arabitol	Deoxy	Ribitol	Xylitol	Erythritol	Threitol
AR0	0	227	94.5	3.5	0.8	0.4	0.6	0.1
AR1	Detected	73	96.7	2.0	0.8	0.1	0.8	0.1
AR5	0	460	93.6	4.2	0.6	0.4	1.1	0.1
AR5-a	99	433	95.1	2.4	1.1	0.4	0.9	0.1
AR5-b	260	390	96.0	1.6	1.2	0.4	0.7	0.1
AR5-c	1005	203	96.7	1.1	0.7	0.6	0.8	0.1
AR5-d	2180	133	97.9	0.6	0.5	0.2	0.7	0.1
AR5-e	4460	69	98.3	0.5	0.6	0.1	0.4	0.1
AR5-f	2000 <sup>c</sup>	163	95.0	3.2	0.4	0.2	1.1	0.1

<sup>a</sup> Reaction conditions: 0.6 g of 5.1% Ru/C catalyst,  $T = 100^{\circ}\text{C}$ , 100 bar of H<sub>2</sub>, 20 wt% aqueous solution of **1** + **2** + **3**.

<sup>b</sup> ppm of sodium anthraquinone-2-sulfonate (with respect to dry substrate).

<sup>c</sup> 2000 ppm of triethylamine.

selectivity to arabitol increased slightly with a concomitant decrease in the formation of deoxy products; however the effect was much smaller than that of A2S addition. Therefore, in addition to the basic ligand effect decreasing dehydroxylation reactions, A2S may well act as a selectivity promoter because of its redox properties, which might block the internal molecular mechanism favoring dehydroxylation reactions.

The data given in Table 9 indicates that upon addition of A2S the largest selectivity increase (from 93.6 to 96.0) was obtained for an addition of 260 ppm or  $0.13 \times 10^{-4}$  mol of A2S. This amount has to be compared to  $2.9 \times 10^{-4}$  mol of ruthenium in the catalyst, or to  $0.9 \times 10^{-4}$  mol of surface ruthenium atoms, given the ca. 30% metal dispersion deduced from particle size measurements. Assuming that all the A2S molecules were adsorbed on the metal surface, the coverage would be 0.14 A2S/Ru<sub>s</sub>.

The hydrogenation experiments discussed above were carried out on the commercial catalyst 5.1% Ru/C presenting comparatively large particle sizes (3–6 nm, Table 2). The effect of A2S addition to arabinonic acid solutions was also studied on the catalyst prepared by cationic exchange, with 1- to 2-nm particle sizes allowing improvement of the selectivity to arabitol, as discussed in Section 3.5. The hydrogenation of AR5 substrate was conducted at 80°C under 100 bar of hydrogen, in the presence of 2000 ppm of A2S. The selectivity to arabitol at 98% conversion was 98.9%. The catalyst was then recycled three times for the hydrogenation of fresh AR5 solutions without adding A2S to the reaction medium. The selectivities to arabitol were close to 99% after each recycling. This indicates that the selectivity of the catalyst was permanently improved, which is probably due to the fact that A2S remains adsorbed on the surface of the catalyst and behaves as permanent modifier.

#### 4. CONCLUSION

This study shows that aqueous solution of arabinonic acid in equilibrium with arabinonolactones are hydrogenated on ruthenium catalysts at 100°C or lower temperatures. The highest selectivity to arabitol was 98.9% at 98% conversion, with a reaction rate of 73 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup> at 80°C. The hydrogenation process can therefore be employed to prepare arabitol from arabinonic acid solution obtained by the oxidative decarboxylation of glucose. Reaction modeling was achieved by a detailed kinetic analysis of reaction data under various reaction conditions. The conversion of substrate follows a rate equation established with the Horiuti–Polanyi mechanism. Individual rate constants for the formation of primary- and secondary-reaction by-products were also determined.

The different factors affecting the selectivity of catalysts to arabitol were analyzed. It was shown that the selectivity is higher on small particles supported on carbon supports. This was attributed to an electron-donating effect of the support on the nanometer-large ruthenium particles, which would decrease the rate of hydrogenolysis or dehydroxylation reactions leading to unwanted deoxy products. The most important factor enhancing the selectivity, because of the decrease of deoxy products, was the presence of anthraquinone-2-sulfonate (A2S), which may be present in residual amounts in solutions obtained from glucose oxidative decarboxylation. With an optimum amount of A2S the selectivity was improved from 93.6 to 96.7%. The adsorbed molecule acts as permanent surface modifier since the catalyst can be recycled with the same improved selectivity without further addition of A2S. The molecule adsorbed on the surface could act as an electron-donating surface ligand decreasing the rate of dehydroxylation reactions.

## ACKNOWLEDGMENT

The Roquette Frères Company is acknowledged for providing financial support for this study, for supplying solutions of arabinonic acid, and for fruitful discussions.

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