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THE SELECTIVE OXIDATION OF ALDOSES AND ALDONIC ACIDS TO 2-KETOALDONIC ACIDS WITH LEAD-MODIFIED PLATINUM-ON-CARBON CATALYSTS

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ABSTRACT

Aldoses and aldonic acids have been oxidised with oxygen and air at 55° in water, using Pt/C catalysts. After oxidation of the reducing group, if available, the primary hydroxyl group is preferentially oxidised using an unmodified catalyst. Addition of a lead(II) salt changes the preference dramatically towards oxidation at the position α to the carboxyl group. Provided that oxygen transfer to the liquid phase is carefully controlled in order to prevent deactivation of the catalyst, 2-ketoaldonic acids can be prepared in high yields.

INTRODUCTION

2-Ketoaldonic acids are formed from aldoses in two steps, namely, aldose→ aldonic acid→2-ketoaldonic acid. Two processes are favoured for the first step, namely, biochemical oxidation and heterogeneous catalytic oxidation with noble metals, preferably palladium. The kinetics of the biochemical route have been described[1,2] and work has been devoted to the use of immobilised enzymes[3–5]. The combined hydrolysis and oxidation of di- and poly-saccharides has been the subject of many investigations[6–10].

The heterogeneous catalytic oxidation of aldose to aldonic acid has been studied in detail[11–15] and is the subject of numerous patents[16–25].

For the second step, numerous biochemically active species have been studied[26,27], but these reactions are slow, requiring reaction times of 12–720 h. Chemical oxidation reactions have been published only in the older literature[28–34], but no catalytic method has been mentioned. Heyns *et al.*[13] stated that almost no selectivity is to be expected for the noble metal-catalysed oxidation of the secondary hydroxyl groups of aldonic acids. We now describe the production of 2-ketoaldonic acids using lead-modified Pt/C catalysts[35,39].

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EXPERIMENTAL

Catalysts. — The Pt/C catalysts were prepared[36] by a modification of the procedure of Zelinskii and Turowa-Pollak[37,38]. After grinding Norit PK 10 × 30 or SX-2 activated carbon, a sieve fraction (72 g) of 50–100 μm was impregnated with 10 g of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6\ H_2O$) in water (200 mL) for 5 h at ambient temperature under nitrogen. The mixture was then cooled to 0°, and the platinum compound was reduced by adding aqueous 35% formaldehyde (170 mL) followed by the slow addition of aqueous 30% KOH (90 mL) during 15 h. In this way, a Pt/C catalyst with a Pt content of ~5% was obtained. A commercial 5% Pt/C catalyst (Degussa, type F 196 RA/W) was also used.

The Pb/Pt/C catalysts were prepared from the Pt/C catalysts by adding lead(II) acetate solutions using just enough water to contain the catalyst and an amount of salt to obtain the required Pb/Pt-ratio.

In order to completely fill the pores of the catalyst with liquid, the suspension was heated until a small part of the water had evaporated, and then allowed to cool. After 18 h, a solution containing 1.8 times the amount of sodium hydroxide or trisodium phosphate necessary to precipitate all the lead was added with vigorous agitation. After 18 h, the catalyst was collected and washed with water until the filtrate was neutral. Initially, the catalyst was dried at 50° under reduced pressure, but later the wet catalyst was used.

The lead content of the $Pb(OH)_2$/Pt/C or $Pb_3(PO_4)_2$Pt/C catalyst was determined gravimetrically as lead(II) chromate after dissolving the lead in 2M nitric acid.

Equipment. — The reactions were carried out with the system shown in Fig. 1. The temperature of the reactor was kept constant to within 0.5°, the pH was regulated by automatic titration with 5M KOH, and the pressure was kept at 0.1 MPa by admitting water from the burette to the oxygen supply vessel. The consumption of alkali and oxygen was monitored as was the oxygen concentration in the liquid.

Procedure. — The desired amount of catalyst, suspended in water (400 mL), was introduced into the stirred batch reactor. A concentrated solution of the substrate at the appropriate pH was added to the supply vessel. Both reactor and supply vessel were then heated to the desired temperature, and the reaction was started as follows. The catalyst suspension and the concentrated substrate solution were heated under nitrogen. After introducing the substrate solution into the reactor, the suspension was kept under nitrogen for 10 min. The stirrer and the nitrogen flow were then stopped, the gas circulation system was quickly evacuated and refilled with oxygen, and the stirrer was restarted. Samples (5 mL) of the reactor mixture, taken with a syringe, were filtered and stored at ~5°. The measured concentrations were corrected for the dilution with KOH and for the effects of sampling.

Unless otherwise stated, the following standard set of reaction conditions was

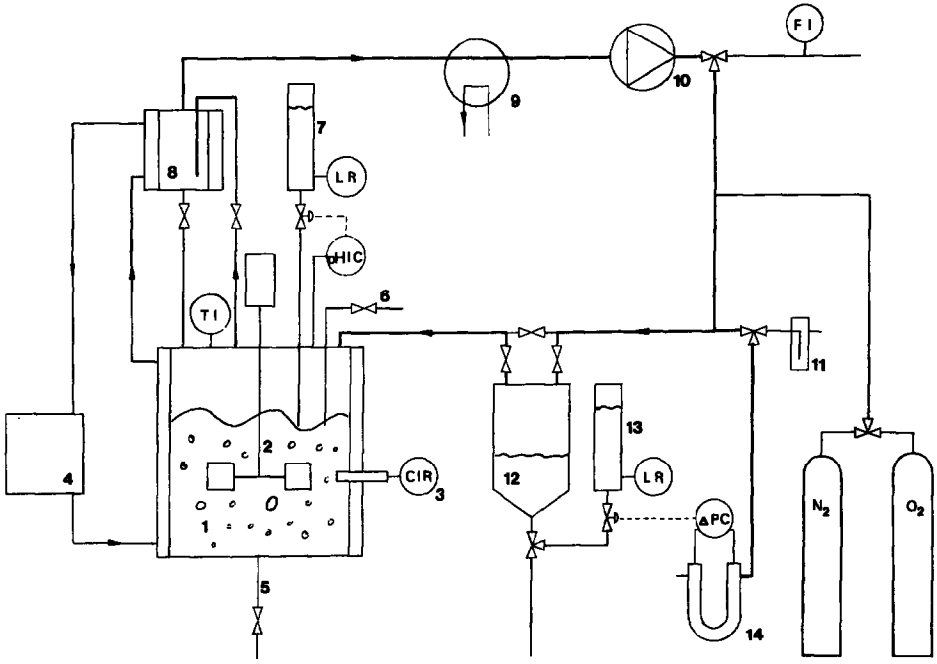


Fig. 1. Flow sheet of the reactor and auxiliary equipment: 1, reactor; 2, turbine stirrer; 3, polarographic oxygen analyser; 4, thermostat; 5, drain; 6, sampling connection; 7, KOH burette; 8, substrate supply vessel; 9, condenser; 10, gas circulation pump; 11, pressure relief; 12, oxygen supply vessel; 13, gas burette; 14, contact manometer for pressure control.

used: pH 8, 55°, [substrate] = 700 mol/m^3, 100% O_2, [$Pb_3(PO_4)_2$/Pt/C catalyst] = 40 kg/m^3, Pb/Pt molar ratio = 0.5.

The conversion (C) and the two selectivities (S) are defined as:

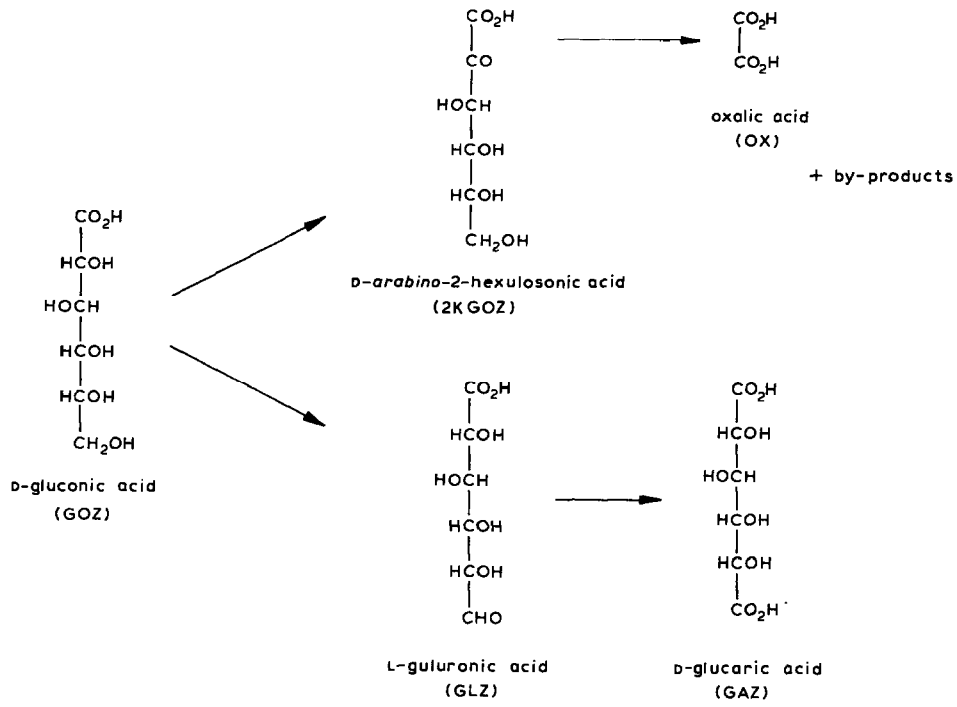
$$C = ([C_{6tot}]_0 - [GOZ])/[C_{6tot}]_0,$$
$$S_2 = [2KGOZ]/([C_{6tot}]_0 - [GOZ]), \text{ and}$$
$$S_6 = ([GLZ] + [GAZ])/([C_{6tot}]_0 - [GOZ]),$$

where $[C_{6tot}]_0$ is the initial concentration of the substrate, and [GOZ], [GAZ], [GLZ], and [2KGOZ] are the concentrations of D-gluconic acid, D-glucaric acid, L-guluronic acid, and D-*arabino*-2-hexulosonic acid (2-keto-D-gluconic acid). The total quantity of material present in the reactor was calculated as an average of the results from the analyses of the second, third, and fourth samples.

RESULTS AND DISCUSSION

Fig. 2 shows the distribution of the main products for the oxidation of D-gluconic acid with a Pt/C catalyst, and Fig. 3 shows the results when a $Pb_3(PO_4)_2$/Pt/C catalyst was used.

The following reaction scheme shows the main products.



Initially, the total carbon balance showed a deficit due to adsorption of the D-gluconic acid on to the catalyst in the nitrogen atmosphere. This acid was desorbed slowly after the nitrogen was replaced by oxygen. For this reason, the selectivities for the two experiments (dotted curves shown in Fig. 4) are not well

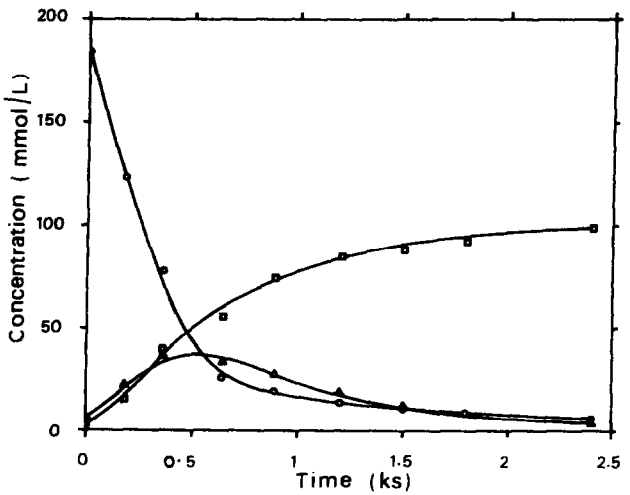


Fig. 2. Main products of the oxidation of D-gluconic acid with a standard Pt/C catalyst, under standard conditions (see Procedure): ○, gluconic acid; △, guluronic acid; □, glucaric acid.

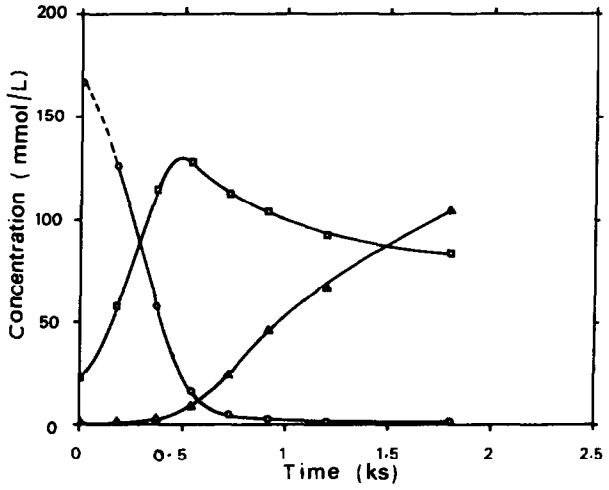


Fig. 3. Main products of the oxidation of D-gluconic acid under standard conditions (see Procedure): ○, gluconic acid; □, *arabino*-2-hexulosonic acid; △, oxalic acid.

defined at the beginning of an experiment. The dramatic change in the selectivities for oxidation at C-2 (S_2) and C-6 (S_6) is shown in Table I.

The ratio of the two selectivities S_2/S_6 increases over 140-fold as a result of the addition of an insoluble lead salt to a platinum-on-carbon catalyst. From a

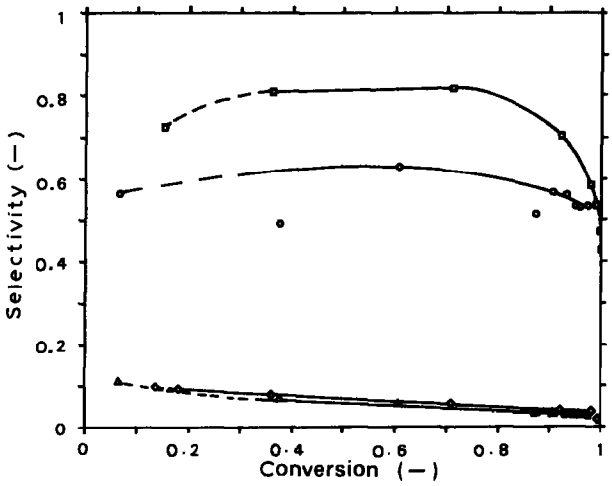


Fig. 4. Comparison of the selectivities S_2 (△, Pt/C; □, Pb/Pt/C) and S_6 (○, Pt/C, ◇, Pb/Pt/C) for the oxidation of D-gluconic acid at C-2 and C-6, respectively, under the standard conditions.

TABLE I

SELECTIVITIES (S) IN THE OXIDATION OF D-GLUCONIC ACID WITH Pt/C AND $Pb_3(PO_4)_2$/Pt/C CATALYSTS AT 50% CONVERSION

	Pt/C	*$Pb_3(PO_4)_2$/Pt/C*
S_2	0.054	0.82
S_6	0.63	0.066
S_2/S_6	0.086	12.4

series of experiments with increasing ratios of Pb/Pt in the catalyst, it was found that a ratio of 0.2 was enough to obtain selectivities for D-*arabino*-2-hexulosonic acid of >90%.

Fig. 5 shows that the selectivity for D-*arabino*-2-hexulosonic acid is somewhat improved when the initial concentration of D-gluconic acid was raised to 1M.

The linearity of the initial parts of the curves of the concentrations of D-gluconic acid in Figs. 2 and 3 shows that the reaction was zero order with respect to D-gluconic acid. In order to ascertain the factor that determined the observed reaction rate, two series of experiments were carried out. The rate obtained using pure oxygen was compared with that for air. Fig. 6 shows that the initial rate in air was ~20% of that in oxygen. Thus, the rate of oxygen transfer from the gas phase to the solution determined the observed rate. When the amount of catalyst was reduced from 40 to 20 to 10 kg/m^3, the initial rate decreased progressively and the catalyst was markedly deactivated. With 40 kg/m^3 of catalyst, a conversion of >95% occurred within 1 ks, conversion at 5 ks was only 75% and 50% using 20 and 10 kg/m^3 of catalyst, respectively. Apparently, the standard conditions are near to

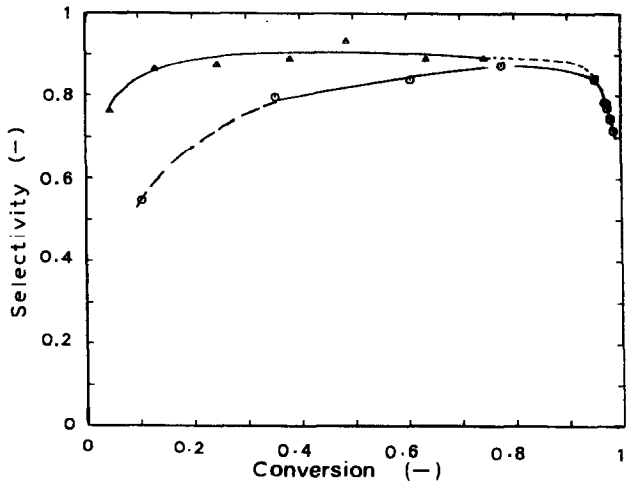


Fig. 5. Comparison of the selectivity S_2 for the oxidation of D-gluconic acid as a function of the initial concentration; other conditions standard. [GOZ]: ○, 500; △, 1000.

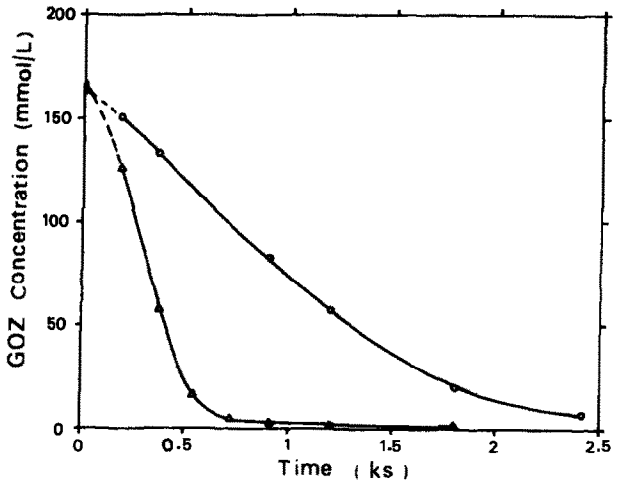


Fig. 6. Concentration of D-gluconic acid as a function of time, using air (O) or oxygen (△); otherwise under the standard conditions.

those where the rate is limited by oxygen transfer. This aspect is being investigated further.

The main by-product of the reaction is oxalic acid produced from D-*arabino*-2-hexulosonic acid (Fig. 3). The other by-products, namely L-guluronic acid and tartaric acid, are formed in small quantities (Fig. 1). The curious form of the curves in Fig. 7 partly reflects the complex reaction mechanism that underlies the formation of these products and partly the deactivation of the catalysts that occurs after about ~500 s (*cf.* Fig. 3).

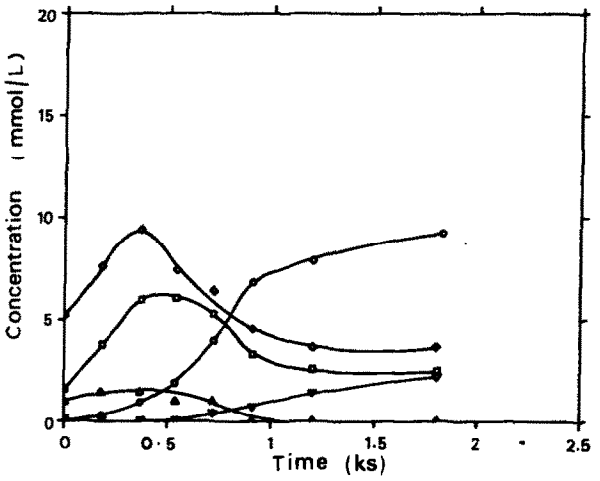


Fig. 7. By-products formed during the oxidation of D-gluconic acid under the standard conditions: △, guluronic acid; ◇, xylo-5-hexulosonic acid; O, tartronic acid; □, glucaric acid; ▽, tartaric acid.

Oxidation of L-gulonic acid, D-glucose, D-galactose, and D-arabinose also gave 2-keto acids. Without optimising these oxidations, the standard conditions, noted above, gave selectivities that ranged from >60% for D-arabinose to 97% for L-gulonic acid. Lactic acid was oxidised rapidly to pyruvic acid with a selectivity of >95%.

Other metals, for example, bismuth and thallium, added to the Pt/C catalyst also bestowed some selectivity for the production of 2-keto acids, but they were not as effective as lead.

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