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CATALYTIC DEHYDROGENATION OF REDUCING SUGARS IN ALKALINE SOLUTION

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ABSTRACT

Aldoses in alkaline medium under the catalytic action of platinum or rhodium are converted into aldonic acids with high selectivity and with concomitant evolution of hydrogen gas. The dehydrogenation reaction has been studied for 25 different mono- and di-saccharides, and is generally applicable for reducing sugars. The influence of several reaction variables has been studied, leading to an adsorption model in which both the negatively charged O-1 and the close contact of H-1 with the catalyst surface are considered to be driving forces for the transfer of hydride from C-1 of the sugar to the catalyst.

INTRODUCTION

Generally, hydrogenation of monosaccharides is performed at elevated temperature and pressure[1–4]. Attempts in our laboratory to hydrogenate monosaccharides under ambient conditions revealed that D-glucose *produced hydrogen* in strongly alkaline medium in the presence of platinum-on-carbon.

It has been reported[5–7] that reducing sugars undergo a Cannizzaro type of reaction in aqueous, alkaline solution in the presence of nickel or platinum under ambient conditions, *i.e.*, a redox reaction of the sugar takes place. In some cases, the oxidation products preponderated together with some formation of hydrogen gas. For instance, D-galactose, D-glucose, and D-arabinose in alkaline medium with Raney nickel gave equimolar amounts of aldonic acid and alditol, whereas, with platinum, more aldonic acid was formed with concomitant production of hydrogen[5]. Hydrogenation of 2-amino-2-deoxy-D-glucose over platinum in alkaline medium gave 1:1 aldonic acid–alditol, whereas the reaction *in vacuo* gave aldonic acid[6]. D-Glucose, D-galactose, D-mannose, and D-arabinose in alkaline medium in the presence of platinum underwent a partial conversion into the respective aldonic acids and alditols, in addition to some production of hydrogen[7].

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In view of these limited data, in contrast to those for the catalytic oxidation of sugars with oxygen[8], we have undertaken a re-investigation[9] involving the activity and selectivity of some heterogeneous catalysts towards the dehydrogenation reaction of aldoses, together with the influence of the configuration of the aldose, the concentration of the alkali and aldose, the solvent, and the temperature. The results allow the formulation of an adsorption model and a mechanism for the dehydrogenation reaction which occurs under very mild conditions with high selectivity.

EXPERIMENTAL

General. — The sugars and 5-hydroxypentanal were commercial products. 2,3,4,6-Tetra-*O*-methyl-D-glucose was prepared by the method of West and Holden[10]. The catalysts 5% Pt/C, 5% Rh/C, 10% Pd/C, and 5% Ru/C were purchased from Drijfhout (Amsterdam). Pt-black was prepared by reduction of a suspension of PtO_2 (Fluka AG) in H_2O with H_2 at 25° and 1 atm.

The reactions were performed at atmospheric pressure in a 50–100-ml reaction vessel, equipped with a thermometer, magnetic stirrer, thermostat mantle (±0.1°), injection rubber, gas-inlet and -outlet tubes, and a revolving, tubular device for adding solids. The gas inlet was connected to a hydrogen burette or to an automatic hydrogenation apparatus[11] that was modified to be able to record both consumption and production of hydrogen gas.

The catalyst and the alkaline solvent (10–20 ml) were placed in the reaction vessel. For experiments at pH <13.5, an anion-exchange resin (Biorad AG1-X2 in the HO^- form, 100–200 mesh; 250 g/litre) was added to keep a constant pH. After evacuation, hydrogen was admitted and this procedure repeated twice. The mixture was stirred for 15–30 min under H_2. The reaction vessel was evacuated and N_2 was admitted; this procedure was repeated twice. The reaction was then started by the introduction of the reactant, either as a concentrated, aqueous solution by injection or as a solid. The reaction was monitored by recording the consumption or production of H_2 (corrected to 25° and 1 atm) as a function of time.

Samples of the reaction mixture were filtered, neutralised with a weakly acidic, cation-exchange resin (Amberlite IRC-50-H-AG, 32–45 mesh, H^+ form) at 0–4°, freeze-dried, and trimethylsilylated [10 mg of dry residue with 0.2 ml of trifluoro-*N*,*O*-bis(trimethylsilyl)acetamide, 0.1 ml of chlorotrimethylsilane, and 0.8 ml of pyridine] for 3–4 h at 25° with vigorous shaking. In some cases, dissolution of the residue was incomplete and the derivatisation was performed at 90°. G.l.c. of the solution thus obtained was performed with a glass column (2.8 m × 2 mm) filled with 5% of QF-1 (50% 3,3,3-trifluoropropylmethylpolysiloxane) on Chromosorb W-HP (80–100 mesh) at 70–90° for 6 min, followed by temperature-programming of 2.5°/min to 200–225°, with N_2 as the carrier gas.

Samples from reactions in $NaOD/D_2O$ or with D-[1-^{2}H]glucose as the reactant were analysed by g.l.c.–m.s. (Varian-Mat 311) or by ^{13}C-n.m.r. spectroscopy (Varian

CFT-20). The gas composition (H_2, HD, D_2) was analysed by m.s. (Varian-Mat SM-1).

Adsorption measurements. — Addition of an equimolar amount of a non-reacting compound during the dehydrogenation reaction of a reactant, in some cases, resulted in a decrease in the rate of hydrogen production. If Δr is the difference in rate (ml of H_2/min) just before the addition (r) and just after the addition of the non-reacting compound, the $\Delta r/r$ value gives an indication about the relative strength of adsorption of that compound with respect to the reactant. In addition, some competitive dehydrogenations of pairs of monosaccharides were carried out by the method previously described[12].

Dehydrogenation of lactose. — A suspension of 5% Pt/C (0.60 g) in 0.33M KOH (60 ml) was stirred for 15 min under H_2 (1 atm) at 25°. After evacuation, N_2 and lactose · H_2O (4.50 g, 13.2 mmol) were introduced into the reaction vessel. The resulting mixture was stirred under a slow current of N_2 for 4.5 h at 25°. The catalyst was filtered off and the aqueous solution was neutralised with a weakly acidic, cation-exchange resin (Amberlite IRC-50-H-AG) at 0–4°. Freeze-drying of the filtered solution yielded potassium lactobionate (4.25 g, 85%; purity, 95%). Dissolving the product in a minimum amount of water, followed by precipitation with methanol, raised the purity to 99%.

RESULTS AND DISCUSSION

Preliminary dehydrogenation experiments. — The attempted hydrogenation of D-fructose, D-mannose, and D-glucose in aqueous, alkaline medium under ambient conditions is shown in Fig. 1. D-Fructose was hydrogenated rapidly and completely to D-glucitol and D-mannitol, the reaction for D-mannose was rather slow and not complete, and D-glucose showed production of hydrogen. If the H_2 atmosphere was displaced by N_2 or argon, the evolution of H_2 gas from D-glucose increased to 0.9 equiv. The main product was D-gluconic acid, in addition to some D-glucitol and

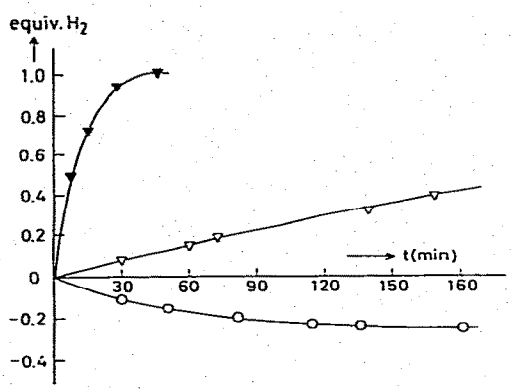


Fig. 1. "Hydrogenation" of D-fructose (▼), D-mannose (▽), and D-glucose (○): 0.07M sugar; 5% Pt/C, 10 g/l; 0.33M KOH; 25°; H_2, 1 atm.

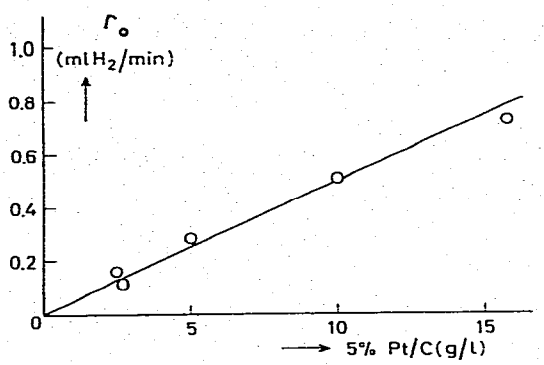


Fig. 2. Initial rate of dehydrogenation (r_0) of D-glucose as a function of the catalyst concentration: 0.07M D-glucose; 0.33M KOH; 5% Pt/C; 25°; N_2, 1 atm.

D-mannitol. Under diminished pressure (0.04 atm) or by purging the solution with N_2 or argon, D-gluconic acid was obtained in 97% yield.

Clearly, it is not correct to denote[5-7] the reaction as a Cannizzaro reaction, since mainly dehydrogenation occurs with some simultaneous hydrogenation as a side reaction.

It may be noted that dehydrogenation of D-glucose under these conditions (Pt/C, 0.33M KOH, 25°) gave D-glucitol–D-mannitol in the ratio 1.83, whereas D-fructose gave D-glucitol–D-mannitol in the ratio 0.77 under the same conditions with H_2. This means that the products of hydrogenation in the D-glucose experiment are formed two-thirds *via* D-fructose and one-third *via* D-glucose. Apart from D-glucose⇌D-fructose interconversion under the strongly alkaline, dehydrogenation conditions, there is also some alkaline degradation of the sugar (a few percent at <35°).

On a preparative scale, using the above-mentioned reaction conditions, lactose could be conveniently converted into potassium lactobionate in good yield (85%).

Kinetics. — The rate of H_2 production at $t = 0$ will be taken as a measure of the initial rate of dehydrogenation r_o. Some hydrogenation of the aldose causes the real dehydrogenation rate to be always somewhat higher than the slope of the plot of H_2 production *versus* time at $t = 0$. This systematic error will be largely eliminated by using relative, instead of absolute, reaction rates for reactions with ≥70% selectivity towards dehydrogenation.

The effect of catalyst concentration on the dehydrogenation rate has been established with D-glucose (Fig. 2). A first-order dependence was found, and, subsequently, the rate of dehydrogenation r_o will be expressed as ml of H_2/min for a catalyst concentration w of 10 g/l.

The influence of $[OH^-]$ on r_o is depicted in Fig. 3. The left-hand plot resembles an acid–base titration curve, indicating that the dehydrogenation reaction occurs *via* the D-glucose anion (G^-). The estimated pK_a value (12.7) corresponds with pK_a values for D-glucose obtained from ^{13}C-n.m.r. and u.v. measurements[13,14]. The right-hand plot shows that, at very high alkalinity (>2M KOH), r_o decreases

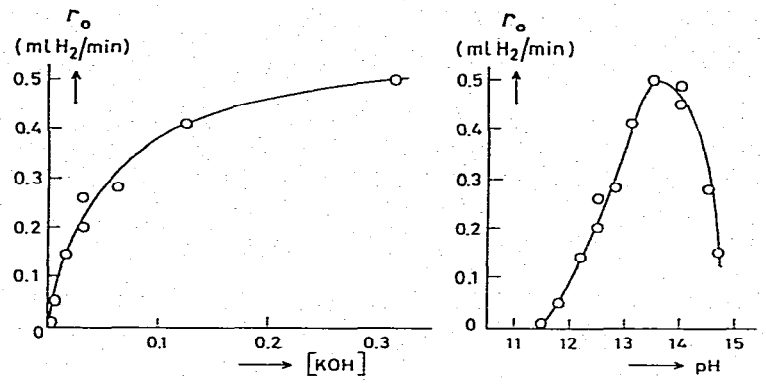


Fig. 3. Influence of hydroxyl-ion concentration on the initial rate of dehydrogenation of D-glucose: 0.06M D-glucose; 5% Pt/C, 10 g/l; 25°; N_2, 1 atm [at pH <13.5 in the presence of Biorad AG 1-X2 (HO^-) resin (250 g/l) as the buffer].

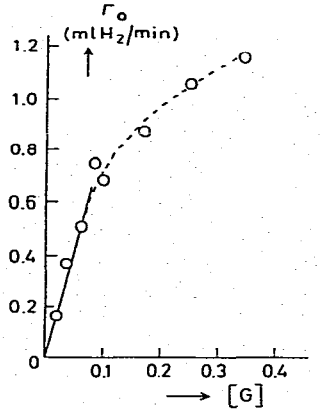


Fig. 4. Initial rate of dehydrogenation *versus* the concentration of D-glucose: 5% Pt/C, 10 g/l; 0.33M KOH; 25°; N_2, 1 atm.

again, which may be due to (weak) co-adsorption of KOH on the catalyst. The order in $[G^-]$ has been investigated by a variation of the total concentration of D-glucose at constant pH (Fig. 4). In the region up to $[G] = 0.1$, D-glucose is almost completely ionised and, therefore, the linear increase of r_o directly reflects a first-order dependence in $[G^-]$. The deviation of the linear correlation for $[G] > 0.1$ is the result of a partial ionisation of D-glucose in that region.

In conclusion, the rate equation $r_o = (dH_2/dt)_{t=0} = k.[G^-].w$ applies to the dehydrogenation reaction.

Table I shows the influence of the reaction temperature on the dehydrogenation of D-glucose on Pt/C. Increase of the temperature causes a higher contribution of hydrogenation. The lower energy of activation of the dehydrogenation reaction (~60 kJ/mol as estimated from Table I), as compared to the D-glucose⇌D-fructose isomeri-

TABLE I

EFFECT OF THE TEMPERATURE ON THE DEHYDROGENATION OF D-GLUCOSE ON PLATINUM[a]

Temperature (degrees)	0	25	50
Initial reaction rate, r_0 (ml of H_2/min)	0.045	0.50	2.25
Selectivity[b]	0.99	0.87	0.81
Reaction time (min)	130	60	15
Product composition (%)			
D-Gluconic acid	94	87	81
D-Glucitol + D-mannitol	1	11	19
D-Glucose	5	1	
Others		1	

[a]0.06M D-Glucose; 5% Pt/C, 10 g/l; 0.33M KOH; N_2, 1 atm. [b]D-Gluconic acid formed/D-glucose converted.

TABLE II

INFLUENCE OF THE CATALYST ON THE DEHYDROGENATION OF D-GLUCOSE[a]

Catalyst	*5% Pt/C*	*5% Rh/C*	*5% Pd/C*	*5% Ru/C*	*Ra-Ni*	*Pt-black*[b]
r_0 (ml of H_2/min)	0.5	1.3	0.1	—	—	0.5
Selectivity	0.9	0.9	0.6	0	0.4	0.9
Equiv. of H_2	0.8	0.8	0.2	—	—	0.8
Conversion (%)	>99	>99	36	13	>99	>99
Reaction time (min)	60	30	90	180	300	60

[a]0.06M D-Glucose; catalyst, 10 g/l; 0.33M KOH; 25°; N_2, 1 atm. [b]5 g/l.

sation in alkaline medium (120 kJ/mol[15]), indicates more D-fructose formation and, consequently, more alditol formation at higher temperature.

Influence of the catalyst. — The activity and selectivity of various catalysts for the dehydrogenation of D-glucose are summarised in Table II. Both Pt/C and Rh/C appear to be the catalysts of choice. Table III shows further that the relative, initial dehydrogenation rates for D-glucose, D-mannose, and D-galactose are quite similar for Pt/C, Pt-black, and Rh/C. Probably, the mechanism of the dehydrogenation reaction is the same for Pt and Rh.

Influence of anions and cations. — The use of Na_2CO_3 as the base results in a high rate of dehydrogenation of D-glucose at a relatively low pH (11–12). For instance, r_o of D-glucose (0.06M; 5% Pt/C, 10 g/litre; 25°; N_2, 1 atm) in the presence of Na_2CO_3 (0.5–2M) at pH = 11.7 amounts to ~0.38 ml of H_2/min, whereas, in the presence of KOH at the same pH, r_o is ~0.05 ml of H_2/min (*cf.* Figs. 5 and 3, respectively). The left-hand plot of Fig. 5 shows a sharp increase of r_o in the region $[Na_2CO_3] < 0.5$M, whilst r_o becomes constant at $[Na_2CO_3] \geqslant 0.5$. In the latter

TABLE III

COMPARISON OF THE DEHYDROGENATION OF D-GLUCOSE, D-MANNOSE, AND D-GALACTOSE ON PLATINUM AND RHODIUM[a]

Aldose	*Catalyst*	r_0 *(ml of H_2/min)*	*Selectivity*	*Equiv. H_2*	*Conversion (%)*	*Reaction time (min)*
D-Glucose	Pt/C	0.5	0.9	0.9	>99	60
D-Mannose		0.1	0.7	0.4	92	180
D-Galactose		0.8	0.9	0.9	>99	30
D-Glucose	Pt-black[b]	0.5	0.9	0.8	>99	60
D-Mannose		0.1	0.7	0.2	50	60
D-Galactose		0.8	1.0	0.9	>99	35
D-Glucose	Rh/C	1.3	0.9	0.8	>99	30
D-Mannose		0.4	0.8	0.1	16	10[c]
D-Galactose		2.4	0.9	0.9	>99	30

[a]0.06M Aldose; 5% metal/support, 10 g/l; 0.33M KOH; 25°; N_2, 1 atm. [b]5 g/l. [c]Production of H_2 ceased after 10 min.

region, however, the pH has attained a constant value; this leads to a linear correlation of r_o with $[OH^-]$ (right-hand plot), which is in accordance with first-order kinetics in $[G^-]$. Complex formation between D-glucose and carbonate ions, favouring ionisation, may explain the high dehydrogenation reactivity at relatively low pH. In this respect, it may be noted that the enolisation of monosaccharides in aqueous Na_2CO_3 also occurs readily[14] as compared to the reaction in aqueous KOH.

The influence of monovalent cations on the dehydrogenation of D-glucose is shown in Table IV. It is obvious that the rate-enhancement in going from Li^+ to

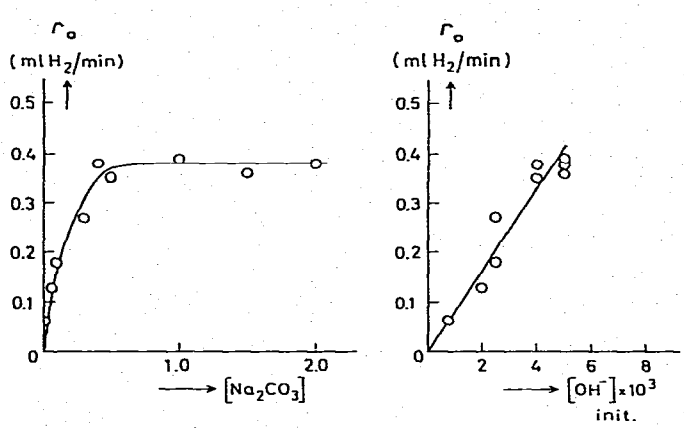


Fig. 5. Influence of Na_2CO_3 as the base on the initial rate of dehydrogenation of D-glucose: 0.06M D-glucose; 5% Pt/C, 10 g/l; 25°; N_2, 1 atm; selectivity, 0.9–1.0.

TABLE IV

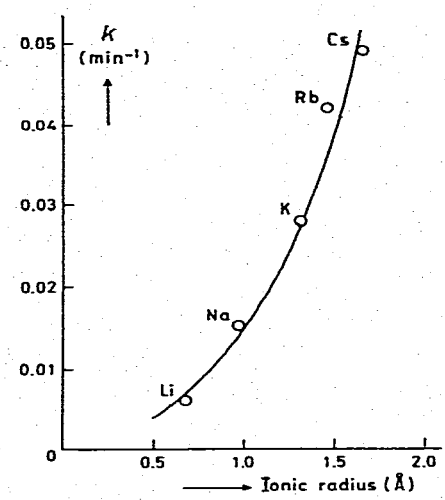
INFLUENCE OF THE CATION ON THE DEHYDROGENATION OF D-GLUCOSE[a]

Base	r_0 *(ml/min)*	k *(min^{-1})*	*Equiv. of H_2*
LiOH	0.14	0.006	0.6
NaOH	0.28	0.015	0.8
KOH	0.45	0.028	0.9
RbOH	0.50	0.042	1.0
CsOH	0.57	0.049	1.0
Me_4NOH	0.14	0.008	0.5

[a]0.06M D-glucose; 5% Pt/C, 10 g/l; 0.33M base; 25°; N_2, 1 atm.

Cs^+ is due to the increase of the cationic radius (Fig. 6), which parallels the ability to disrupt the water structure[16]. In this respect, it may be noted that both NMe_4^+ and Li^+ possess a large, primary zone, because of the apolar alkyl groups and a strong, primary hydration mantle, respectively, and that they act as promoters of water structure. Disruption of the water structure will partly disturb the hydration mantle around the sugar anion and thus favour the necessary interaction of the sugar anion and the catalyst for reaction. This picture is consistent with the effect of alcohol–water mixtures on the dehydrogenation reaction (see below).

Use of mixed solvents. — The influence of methanol–water mixtures on the



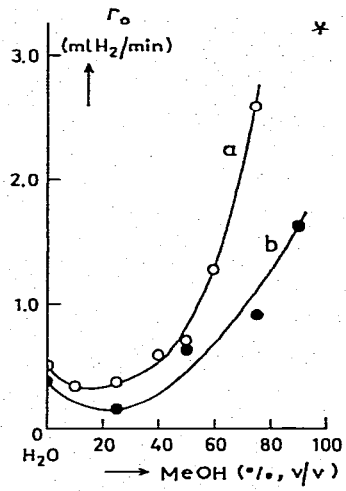
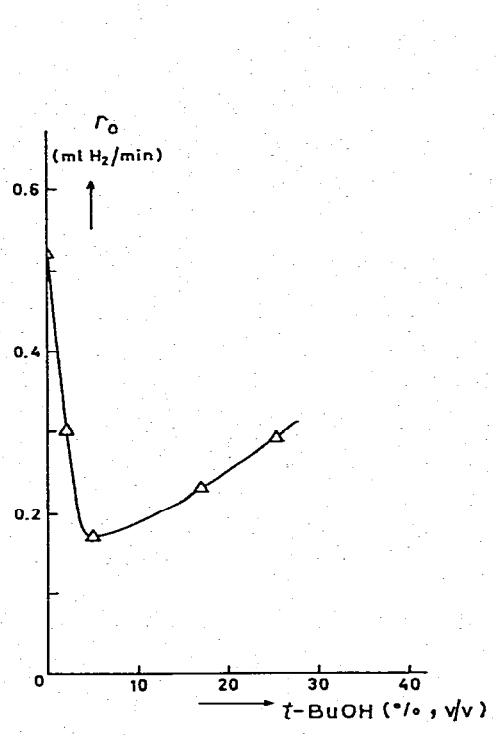


Fig. 6. Effect of the cation on the dehydrogenation rate of D-glucose: 0.06M D-glucose; 0.33M MOH; 5% Pt/C, 10 g/l; 25°; N_2, 1 atm.

Fig. 7. Dehydrogenation of D-glucose (0.06M) in methanol–water mixtures: 5% Pt/C, 10 g/l; 25°; N_2, 1 atm; (*a*) 0.33M KOH (★ = 13.2mM KOH), (*b*) 2M Na_2CO_3 (or saturated in the case of higher percentages of MeOH); selectivity, 0.9–1.0.



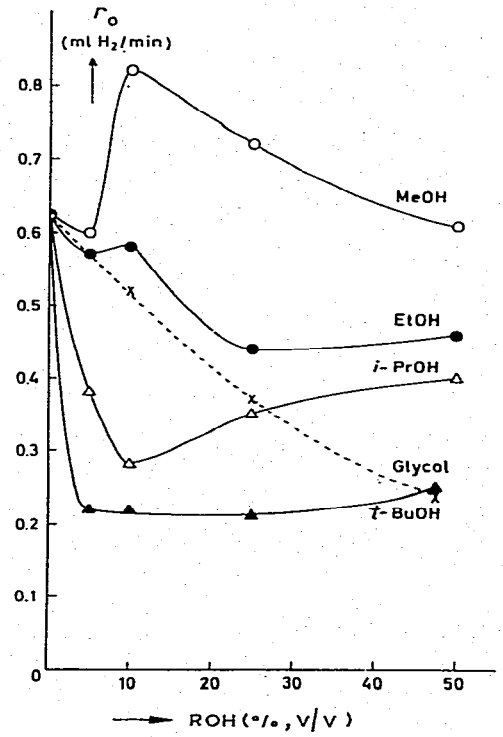


Fig. 8. Dehydrogenation of D-glucose (0.06M) in *tert*-butyl alcohol–water mixtures: 5% Pt/C, 10 g/l; 25°; N_2, 1 atm.

Fig. 9. Dehydrogenation of lactose (0.08M) in alcohol–water mixtures: 5% Pt/C, 10 g/l; 0.33M KOH; 25°; N_2, 1 atm.

dehydrogenation of D-glucose with KOH or Na_2CO_3 as the base is shown in Fig. 7. The rate of dehydrogenation initially decreased on addition of methanol, up to ~20% v/v. However, further increase in the percentage of methanol enhanced the rate substantially. An analogous picture was obtained for D-mannose and D-galactose. The addition of *tert*-butyl alcohol caused a greater, initial decrease in reaction rate (Fig. 8), in line with other reactivity studies for alcohol–water mixtures[16].

For comparison, the influence of various alcohol–water mixtures on the dehydrogenation of lactose has been examined (Fig. 9). The relative order MeOH > EtOH > i-PrOH > *t*-BuOH is in accordance with the results for D-glucose. However, the absolute influence of each alcohol differs for the two sugars and makes difficult an explanation of the solvent effects. The making and breaking effects on water structure by alcohols, at relatively low and high concentration, respectively, are well known[16]; furthermore, the hydration of sugars and their anions will be affected by the addition of alcohols to an aqueous solution[17]. Taking into account that the sugar itself also acts as an alcohol[18], as may be reflected by the effect of glycol in Fig. 9, and that the sugar molecules mutually influence their reactivities, the apparent

TABLE V

INFLUENCE OF THE ALDOSE STRUCTURE ON THE DEHYDROGENATION[a]

Aldose	*Relative, initial rate*	*Selectivity*[b]	*Equiv. of H_2*	*Conversion (%)*	*Reaction time (min)*
Glycolaldehyde[c,d]	—	0	—	90	300
D-Glyceraldehyde[d]	—	0	—	90	180
D-Erythrose[c]	—	0	—	10	180
D-Ribose	0.2	0.7	0.4	>99	180
L-Arabinose	0.6	0.8	0.6	>99	120
D-Xylose	0.3	0.7	0.4	97	180
D-Lyxose	—	0.5	—	25	60
D-Allose	0.5	0.9	0.6	79	180
D-Altrose	0.2	0.8	0.3	50	180
D-Glucose	1.0[e]	0.9	0.9	>99	60
D-Mannose	0.2	0.7	0.4	92	180
D-Galactose	1.7	0.9	0.9	>99	30
D-Talose	0.4	0.7	0.4	>99	180
2-Deoxy-D-*arabino*-hexose	0.4	0.7	0.4	>99	180
6-Deoxy-D-glucose	0.8	0.9	0.7	82	90
3-*O*-Methyl-D-glucose	0.6	0.9	0.8	97	180
2,3,4,6-Tetra-*O*-methyl-D-glucose	0.8	0.9	0.9	98	180
2-Amino-2-deoxy-D-glucose	0.5	0.9	0.8	>99	180
2-Deoxy-D-*lyxo*-hexose	0.7	0.9	0.6	>99	90
6-Deoxy-D-galactose	1.1	0.9	0.9	>99	90
Cellobiose	0.6	0.9	0.9	>99	180
Maltose	1.1	0.9	0.8	>99	60
Lactose	1.7	1.0	1.0	>99	30
D-Glucuronic acid	0.2	—[f]	0.4	—[f]	300
D-Galacturonic acid	0.3	—[f]	0.6	—[f]	180
5-Hydroxypentanal[g]	—	0	—	0	180

[a]0.06M aldose; 5% Pt/C, 10 g/l; 0.33M KOH; 25°; N_2, 1 atm. [b]Aldonic acid formed/aldose converted. [c]Also no production of H_2 with 5% Rh/C (10 g/l). [d]Also no production of H_2 at 50°. [e]0.5 ml of H_2/min. [f]Reaction product not analysed. [g]Also no production of H_2 in 75% MeOH.

difference between the three monosaccharides on the one hand and the disaccharide lactose on the other is understandable. The retardation generally found at low concentration of alcohol has its possible origin in the making effect on water structure, leading to a more-stable water mantle around the sugar anion by which it becomes less accessible to the catalyst.

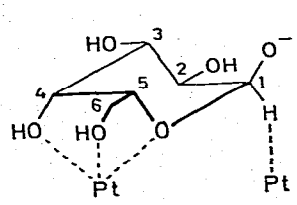
Carbohydrate structure and reaction mechanism. — The reaction rate and the selectivity of the dehydrogenation over 5% Pt/C are dependent on the configuration of the aldose (Table V). Aldopentoses, aldohexoses, and the disaccharides cellobiose, lactose, and maltose are all dehydrogenated. On the other hand, glycolaldehyde, D-glyceraldehyde, and D-erythrose were not dehydrogenated, as was the case for such other (non-sugar) aldehydes as 2-furaldehyde, benzaldehyde, and 5-hydroxy-

pentanal. Apparently, a pyranoid structure is necessary for dehydrogenation. In addition, non-anomeric hydroxyl groups are required, as shown by the fact that 5-hydroxypentanal (almost completely present in the pyranoid structure) does not react under the present conditions.

Comparison of the reactivity for the various pentoses and hexoses indicates the following structural effects: (*a*) an axial HO-4 group has a rate-enhancing effect (*cf.* r_0 for D-galactose and D-glucose, L-arabinose and D-xylose, D-talose and D-mannose, and D-ribose and D-lyxose); (*b*) an axial HO-2 group has a retarding effect (*cf.* r_0 for D-galactose and D-talose, D-glucose and D-mannose, L-arabinose and D-ribose, and D-xylose and D-lyxose); (*c*) the position of HO-3 is of less importance: D-mannose and D-altrose have the same r_0, and D-allose reacts somewhat slower than D-glucose; (*d*) replacement of the CH_2OH group by H results in a decrease of r_0, (*cf.* r_0 for L-arabinose and D-galactose, D-xylose and D-glucose, D-ribose and D-talose or D-allose, and D-lyxose and D-mannose).

The influence of an HO-6 group is further shown by the somewhat lower reactivities of 6-deoxy-D-glucose and 6-deoxy-D-galactose in comparison with those of D-glucose and D-galactose, respectively. A carboxyl group at position 6 has a retarding effect (*cf.* r_0 for D-glucuronic acid and D-galacturonic acid with r_0 for D-glucose and D-galactose, respectively). The unfavourable effect of an axial HO-2 group is further shown by the higher reactivity of 2-deoxy-D-*arabino*-hexose compared with that of D-mannose. On the other hand, the absence of an equatorial HO-2 group retards the reaction (*cf.* r_0 for 2-deoxy-D-*arabino*-hexose and 2-deoxy-D-*lyxo*-hexose with r_0 for D-glucose and D-galactose, respectively). The methyl glycosides were not dehydrogenated, as would be expected from the foregoing, whereas methylation of the other hydroxyl groups had a minor influence on r_0 (*cf.* 2,3,4,6-tetra-*O*-methyl-D-glucose and D-glucose).

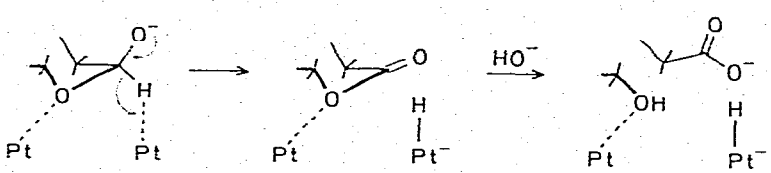
The various structural effects on r_0 may be summarised as follows: HO-4*a* > HO-4*e*; HO-2*e* > H-2 > HO-2*a*; HO-3*e* ≥ HO-3*a*; and, at position 6, CH_2OH > CH_3 > H > CO_2^-. These structural influences on the rate of dehydrogenation may be the result of differences in strength of adsorption as well as in reactivity of the adsorbed aldose-anions. In view of the data in Table V, we postulate a mode of adsorption of the sugar anion on the catalyst surface, leading to reaction, which is depicted below for D-galactose.

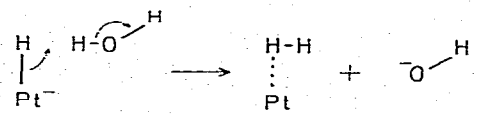


As shown by molecular models, the α-D-galactose anion fits quite well on the (111), (100), and (110) planes of platinum. The sugar anion adsorbs through O-4, O-5, and O-6 on the catalyst surface as a tridentate ligand in which H-1 is favourably

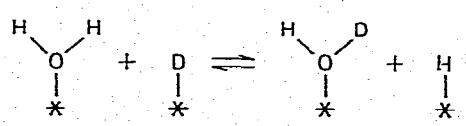
located for abstraction. Furthermore, in this mode of adsorption, an axial H-2 is close to the catalyst surface, which explains the unfavourable effect of an axial HO-2 group by van der Waals repulsion between O-2 and Pt. The position of the HO-3 group is less relevant, since this hydroxyl group cannot interact seriously with the platinum. The lack of an axial HO-4 and/or CH_2OH group at position 6 gives a less-efficient adsorption of the sugar anion on the catalyst surface for the abstraction of hydrogen and thus results in a decrease of reaction rate. Further evidence for this model has been gained by competitive dehydrogenations involving pairs of sugars (or derivatives) (see below).

Comparison of r_o of D-glucose and D-[1-^{2}H]glucose on Pt reveals a kinetic H/D isotope effect of 5. Breaking of the C-1–H-1 bond is apparently the rate-limiting step of the dehydrogenation reaction. Dehydrogenation of D-[1-^{2}H]glucose (0.07M; 5% Pt/C, 8.6 g/l; 0.33M KOH; 25°; N_2, 1 atm) did not lead to incorporation of deuterium into D-gluconic acid, whereas D-[1-^{2}H]glucitol was formed selectively. It is concluded that the driving force for abstraction of hydrogen is a negatively charged O-1 in combination with the favourable position of H-1 towards the platinum. We envisage a hydride transfer from the aldose anion towards the platinum surface, reaction of the hydrido-platinum species with water to give hydrogen gas and hydroxide, and subsequent, rapid hydrolysis of the resulting lactone in the alkaline medium to give the free carboxylate.





The gas evolved from D-[1-^{2}H]glucose (see above; reaction time, 180 min) consisted of ~70% of H_2 and ~30% of HD; dehydrogenation of D-glucose in 0.33M NaOD under the same conditions gave ~85% of D_2 and ~15% of HD. The reaction mechanism presented would predict selective formation of HD in both cases. The discrepancy, however, is caused by fast H/D exchange between hydrogen (or deuterium) and the solvent on the platinum surface, *e.g.*,



The occurrence of such an exchange reaction has been established for neutral and acid media[19].

Adsorption phenomena on the catalyst. — In order to gain insight into the extent to which dehydrogenation is retarded by the reaction products, some competition experiments were performed. The relative decrease in rate of dehydrogenation upon addition of equimolar amounts of D-glucitol, D-gluconate, and D-mannitol to an alkaline, aqueous solution of D-glucose in the presence of Pt/C was rather small. This means that no serious co-adsorption of the reaction products on Pt occurs.

Addition of an equimolar amount of methyl α-D-galactopyranoside to the D-glucose dehydrogenation reaction over Pt retarded the reaction more ($\Delta r/r = 0.3$) than the addition of the same amount of methyl α-D-glucopyranoside ($\Delta r/r = 0.1$). This is in accordance with the favourable geometry of the D-galactose molecule for adsorption on platinum, in which the axial HO-4 group plays an important role. This adsorption model, leading to reaction, is further supported by the following orders in strength of adsorption of the aldose anions: D-galactose > D-glucose > D-mannose, D-talose > D-mannose, D-glucose > D-xylose, and D-galactose > 6-deoxy-D-galactose, as determined by competitive dehydrogenation of pairs of the hexoses. It has to be noted that the experimental differences in rate of dehydrogenation, as determined by the competition method, may be affected to some extent by the differences in the kinetic rate constants.

CONCLUSION

Platinum and rhodium are suitable catalysts for the dehydrogenation of aldopentoses, aldohexoses, and reducing disaccharides. The very mild conditions as well as the high selectivity of the reaction enable it to be used for the preparation of aldonic acids. In addition, the dehydrogenation reaction provides a convenient procedure for transfer hydrogenations with, for example, D-glucose as the hydrogen donor[9]. A study of the transfer hydrogenation of invert sugar will be published elsewhere.

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