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# CATALYTIC DEHYDROGENATION OF REDUCING SUGARS IN ALKALINE SOLUTION AT AMBIENT CONDITIONS. TRANSFER HYDROGENATION OF FRUCTOSE.

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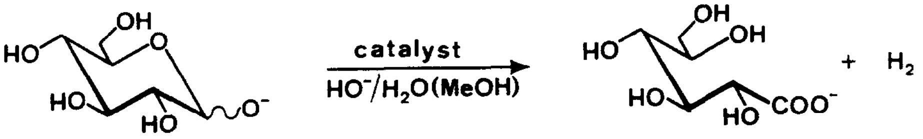
In the 1930's literature[1], it is reported that an aqueous alkaline solution of a reducing sugar in the presence of nickel or platinum results in a Cannizzaro type of reaction, *i.e.* a redox reaction of the sugar takes place. In some cases, however, the oxidation products predominated together with some formation of hydrogen gas. In view of the limited data available and the fact that this very interesting reaction has not received any further attention in the literature, in contrast to the catalytic oxidation of sugars with oxygen[2], we have undertaken a reinvestigation.

We have found that in alkaline medium under ambient conditions in the presence of transition metals, aldoses can be converted to their sugar acids with high selectivity and with concomitant production of hydrogen gas. For example, glucose gave excellent results when platinum or rhodium was used as the catalyst (Table 1).

Table 1. Alkaline glucose dehydrogenation[a]



| Catalyst | Solvent | Temperature ($^oC$) | Selectivity[b] | Conversion (%) | Time (h) |
|---|---|---|---|---|---|
| 5% Pt/C | $H_2O$ | 0 | 0.99 | 95 | 2.10 |
| 5% Pt/C | $H_2O$ | 25 | 0.87 | 97 | 1.00 |
| 5% Pt/C | $H_2O$ | 50 | 0.81 | 99 | 0.25 |
| 5% Pt/C | 75% MeOH | 25 | 0.99 | 97 | 0.67 |
| 5% Rh/C | $H_2O$ | 0 | 0.96 | 100 | 1.33 |
| 5% Rh/C | $H_2O$ | 25 | 0.95 | 100 | 0.50 |
| 5% Rh/C | 75% MeOH | 25 | 0.89 | 89 | 0.50 |

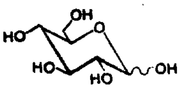
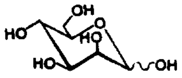
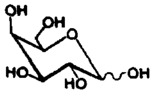
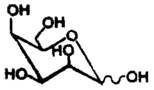
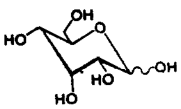
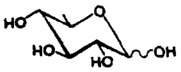
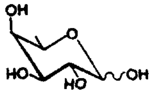
[a] glucose, 0.07 mole/l; catalyst, 10 g/l; KOH, 0.33 mole/l; 1 atm $N_2$

[b] gluconic acid formed / glucose converted

Other transition metals, *e.g.* Raney-nickel, palladium, ruthenium, were less active and showed much lower selectivity. With platinum and rhodium as the catalyst, only small amounts of by-products were formed from glucose due to isomerization (to fructose), alkaline degradation (to lactic acid), and hydrogenation (to glucitol and mannitol). On platinum ($H_2O$, $25^{\circ}$), the reduction products were formed from both glucose (38%) and fructose (62%) as determined by the glucitol/mannitol ratios found in the dehydrogenation of glucose (1.83) and in the hydrogenation of fructose (0.77) under the same reaction conditions.

In aqueous medium with platinum as the catalyst, the dehydrogenation of glucose is first order in catalyst ($< 15$ g/l), in glucose ($< 0.1$ mole/l), and in hydroxide ($12 < pH < 13$). Clearly, the reaction proceeds *via* the glucose anion (apparent $pK_a \approx 13.5$ under these conditions as determined by $^{13}C$ NMR[3]), whereas the C-H bond breaking is the rate-determing step as indicated by a kinetic isotope effect $k_{glucose}/k_{glucose\text{-}1\text{-}d} = 6$. Furthermore, the dehydrogenation is retarded by the reaction products as they are formed in increasing amounts. This is due to co-adsorption of the products on the catalyst surface, as determined by some exploratory competition experiments[4], with

Table 2. Influence of hexose structure[a]

| Hexose | | Relative initial rate | Selectivity[b] |
|---|---|---|---|
| glucose |  | 1.0 | 0.87 |
| mannose |  | 0.2 | 0.71 |
| galactose |  | 1.7 | 0.92 |
| talose |  | 0.4 | 0.68 |
| allose |  | 0.7 | 0.91 |
| 6-deoxyglucose |  | 0.8 | 0.94 |
| 6-deoxygalactose |  | 1.1 | 0.94 |

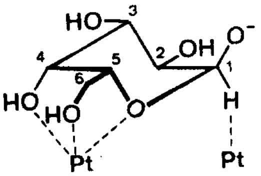
[a] hexose, 0.07 mole/l; 5% Pt/C, 10 g/l; 0.33 N aqueous KOH; $25^{\circ}$; 1 atm $N_2$

[b] aldohexonic acid formed / hexose converted

adsorption constants $b_{glucitol} \approx 0.4$ and $b_{gluconate}$, $b_{mannitol} < 0.1$, with respect to the glucose anion.

As shown in Table 2 for a series of hexoses, both the reaction rate and the selectivity of the dehydrogenation reaction on platinum are rather dependent on the configuration of the aldose. Comparison of mannose with glucose and of talose with galactose shows that a 2-OH group in axial position retards the reaction. On the other hand, a 4-OH group in axial position has an accelerating effect as shown by the higher rates for galactose and talose in comparison with glucose and mannose, respectively. The position of the 3-OH group is of minor importance. Replacement of the 6-$CH_2OH$ group by H results in a decrease of reaction rate as indicated by comparison of configurationally related pentoses and hexoses, *e.g.* ribose/allose ≈ 0.3, xylose/glucose ≈ 0.3, and lyxose/mannose < 0.3. Finally, the influence of the 6-OH group is demonstrated by the lower rates of reaction of 6-deoxyglucose and 6-deoxygalactose with respect to the parent hexoses.

These phenomena point to a mode of adsorption of the sugar anion on the platinum surface, leading to reaction, which is depicted below for galactose.

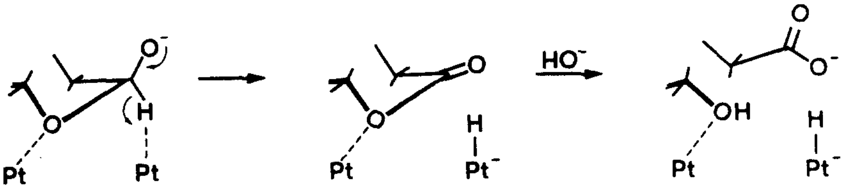


As shown by molecular models, the galactose anion in its α-configuration fits quite well on the 111, 100, and 110 planes, in which the sugar anion through O-4, O-5, and O-6 adsorbs on the platinum surface as a tridentate ligand and the hydrogen at C-1 is favourable located for abstraction. The axial 2-H atom is close to the catalyst surface which explains the unfavourable effect of an axial 2-OH group by van der Waals repulsion between O-2 and Pt. The position of the 3-OH group is less relevant, since this hydroxyl cannot give any serious interaction with the platinum. The lack of an axial 4-OH and/or a 6-$CH_2OH$ group gives a less efficient fixation of the sugar anion on the catalyst for the H-abstraction and thus results in a decrease of reaction rate. Consequently, this model would imply the following orders in strength of adsorption:

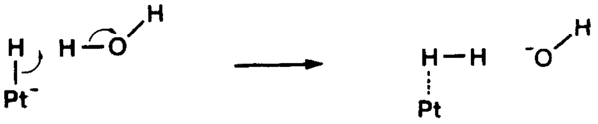
(i) galactose > glucose > mannose
(ii) talose > mannose
(iii) glucose > xylose
(iv) galactose > 6-deoxygalactose.

These orders, indeed, were established experimentally from competitive dehydrogenations of pairs of the hexoses. In addition, the rather strong adsorption of methyl α-galactoside (b = 0.4 relative to the glucose anion) with respect to methyl α-glucoside (b < 0.1) further supports the favourable geometry of the galactose molecule for adsorption on platinum, in which the axial 4-OH group plays an important role.

The driving forces for the transfer of the hydride from C-1 towards the platinum are both the negatively charged O-1 atom and the close contact of H-1 to the platinum. Rapid hydrolysis of the lactone primarily formed gives the free carboxylate.



Concomitantly, the chemisorbed hydride species reacts with water to hydrogen gas and hydroxide.



It may be noted that this very mild dehydrogenation reaction offers a potential convenient procedure for transfer hydrogenations with glucose as hydrogen donor. As an example, we have applied such a procedure for the reduction of fructose. Reaction of a 1:1 mixture of glucose and fructose (invert sugar) in 0.33 N aqueous KOH with 5% Pt/C at 25° gave 51% gluconic acid and 49% glucitol/mannitol (0.77:1) without by-products. Evolution of hydrogen gas did not occur and fructose was completely converted. No enantiomeric induction could be observed (hydrogenation of fructose under the same conditions gave an identical glucitol/mannitol ratio), *i.e.* the abstracted hydride species has lost its "chirality" on the platinum surface.

Further studies concerning the mechanism and the scope and limitations of these dehydrogenation and hydrogen transfer reactions are in progress.

## References

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[3] *Cf.* G. de Wit, A.P.G. Kieboom, and H. van Bekkum, Tetrahedron Lett. 1975, 3943.

[4] *Cf.* H. van Bekkum, A.P.G. Kieboom, and K.J.G. van de Putte, Recl. Trav. Chim. Pays-Bas 88, 52 (1969).