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$RuCl_2(PPh_3)_3$-catalyzed transfer hydrogenation of D-glucose

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Abstract

Glucose is transfer hydrogenated by propan-2-ol, butan-2-ol, cyclohexanol, benzyl alcohol, 1-phenylethanol, benzhydrol, 2-methoxyethanol and tetrahydrofurfuryl alcohol in the presence of $RuCl_2(PPh_3)_3$ at 100 °C and atmospheric pressure. Mixed solvent systems such as dimethylacetamide–water and dioxane–water are utilized for this reaction. The major product from glucose is sorbitol, although glucono-1,5-lactone is invariably formed as a side product from a disproportionation reaction. When 2-methoxyethanol and tetrahydrofurfuryl alcohol are used as hydrogen donors, the catalyst undergoes permanent change to a hydridocarbonyl complex, which catalyzes only disproportionation of glucose. Glucose also acts as a good hydrogen donor when hydrogen acceptors such as cyclohexanone are introduced into the reaction system.

Introduction

Transfer hydrogenation, an interesting alternative to conventional catalytic hydrogenation, is receiving much importance in recent years [1–3]. This reaction, promoted by both homogeneous and heterogeneous catalysts, permits the reduction of a wide variety of functional groups by different hydrogen donors. With respect to sugars, only a few articles on transfer hydrogenation catalyzed by heterogeneous catalysts are published in the literature [4–7]. The first paper on this subject [4] gives the details of Raney Ni-catalyzed transfer hydrogenation of glucose to sorbitol by tetralin and cyclohexanol. The reduction of glucose with tetralin has been carried out in pyridine since it can dissolve glucose and also mix with tetralin. In the case of cyclohexanol, the sorbitol formed has a tendency to gelatinize, thus making the reaction mixture viscous and inhibiting the reaction. Tetrahydrofurfuryl alcohol, a reasonably good solvent for glucose, has also been successfully used as a hydrogen donor [5, 6]. Karbinos and Ballum [7] have utilized ethanol as a hydrogen donor for glucose reduction which is catalyzed by Raney Ni.

Homogeneous transfer hydrogenation of glucose catalyzed by $RuCl_2(PPh_3)_3$ was first reported by our research group [8, 9]. Various alcohols such as propan-2-ol and butan-2-ol were found to be good hydrogen donors. It has been observed that when hydrogen donors are not efficient or when

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the catalyst is not very active or when bases are added to the reaction medium, glucose undergoes disproportionation to sorbitol and glucono-1,5-lactone. Such a reaction is known to be catalyzed by both heterogeneous catalysts and strongly basic compounds. For example, glucose underwent a redox reaction in the presence of Raney Ni and 2% NaOH [5] and Pt [10].

In addition to accepting hydrogens, glucose can also donate them to other unsaturated compounds, proving itself a good hydrogen donor. Such a process utilizing glucose as hydrogen donor is already available in heterogeneously catalyzed reactions. For instance, transfer hydrogenation of cyclohexanone, acetone, maleic acid, cinnamic acid, nitrobenzene [11], α-acetamido-β-phenylacrylic acid [12] and fructose [13, 14] by glucose in the presence of Raney Ni and Pt have been reported. Glucose is oxidized to gluconic acid except in the case of nitrobenzene, where it decomposes. Regarding homogeneous catalysis, Descotes *et al.* have extensively used substituted sugars to reduce various functional groups in the presence of transitional metal complexes [15–17]. Transfer hydrogenation of cyclohexanone to cyclohexanol utilizing glucose as hydrogen donor in the presence of $RuCl_2(PPh_3)_3$ has been reported [9].

In this article, the results of transfer hydrogenation of glucose by propan-2-ol, butan-2-ol, cyclohexanol, benzyl alcohol, 1-phenylethanol, benzhydrol, 2-methoxyethanol and tetrahydrofurfuryl alcohol are presented. The hydrogen donating ability of glucose under the catalytic influence of $RuCl_2(PPh_3)_3$ is also demonstrated.

Experimental

D-Glucose (Pfizer), sorbitol (Koch-Light), $RuCl_3 \cdot xH_2O$ (Johnson Matthey Chemicals), PPh_3 (Ventron) and benzhydrol (Koch-Light) were used as received. $RuCl_2(PPh_3)_3$ [18], $RuHCl(CO)(PPh_3)_3$ [19], $RuH_2(PPh_3)_4$ [19] and $RuH_2(CO)(PPh_3)_3$ [20] were prepared according to the literature. All solvents and hydrogen donors except 1-phenylethanol (Fluka) and dimethylacetamide (Koch-Light) were obtained from BDH (AnalaR grade). These liquids were purified by standard methods [21] and stored under nitrogen for further use. Ultra high pure (UHP) hydrogen and nitrogen (Indian Oxygen) were used throughout this work.

The experimental set-up consisted of a specially designed double-walled glass vessel of 75 ml capacity provided with a mechanical stirrer, a gas inlet, a double surface condenser, a thermometer well and a manostat. Glucose, deaerated hydrogen donor and solvents were taken in the inner portion of the vessel and heated to 100 °C with the help of butan-2-ol vapor. The catalyst was then added to the solution under nitrogen atmosphere. A positive pressure of an inert gas (N_2) was always maintained over the reaction medium to avoid exposure to O_2 atmosphere.

The estimation of unreacted glucose was achieved with the aid of Fehling's solution [22]. Interference due to sorbitol, glucono-1,5-lactone, hydrogen

donors, dehydrogenated products and catalysts were verified and found to be negligible. Thin-layer and gas chromatographies were used to separate the reaction products, and IR spectroscopy to characterize the products and catalysts. The instruments employed for this purpose were a gas chromatograph (Varian model 1800) equipped with a thermal conductivity detector (TCD) and 20% Carbowax 20M on Chromosorb P (80/100 mesh) column (18 ft× $\frac{1}{8}$ in) and an IR spectrophotometer (Perkin-Elmer 257).

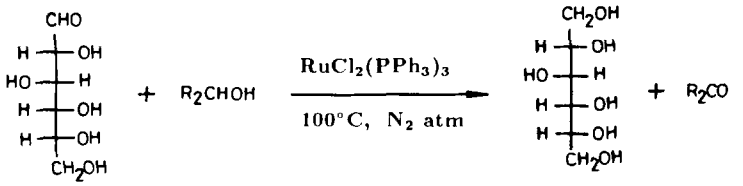
Results and discussion

Mixed solvent systems were exploited for transfer hydrogenation of glucose, because selecting a single solvent for both substrate and the catalyst is a difficult proposition. Thus dimethylformamide (DMF) and dimethylacetamide (DMA) were used as solvents for the catalyst and water was chosen for glucose.

Transfer hydrogenation by propan-2-ol and butan-2-ol

Transfer hydrogenation of glucose by various hydrogen donors (general formula R_2CHOH) is represented in Scheme 1. The percent conversions of glucose in DMF–alcohol–water and DMA–alcohol–water systems, where alcohol is either propan-2-ol or butan-2-ol, are given in Table 1. From the conversion results, it is obvious that DMF has an inhibiting effect on the overall reaction. The most likely explanation for this effect is that DMF blocks the coordination sites which are otherwise required by the aldehyde form of glucose for the desired reaction to take place. Free coordination sites, or sites which can be generated by easy displacement of ligands, are most important here, since the equilibrium concentration of aldehydo–glucose is very low [23].

The dehydrogenated products of propan-2-ol and butan-2-ol, namely, acetone and butanone, were identified by gas chromatography. It is clear from Table 1 that the selectivity to sorbitol is not 100%, *i.e.*, a side product, glucono-1,5-lactone, is formed as a result of disproportionation (Scheme 2). The extent of this competing reaction can be determined by estimating the dehydrogenated products of hydrogen donors (acetone and butanone). Partial loss of these low boiling ketones during reaction made their determination unreliable. Alternatively, sorbitol and glucono-1,5-lactone were estimated by



Aldehydo-glucose Sorbitol

Scheme 1. Transfer hydrogenation of glucose by various alcohols.

TABLE 1

Transfer hydrogenation of glucose by various alcohols[a]

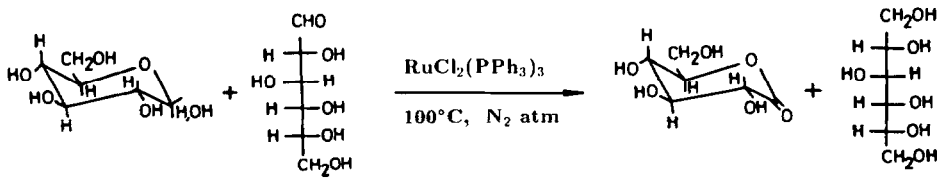
Hydrogen donor and solvents	[H-donor]/[glucose]	Glucose conv. (%)	Selectivity[b] (%)
propan-2-ol–DMF–water (18:4:3)[c]	47.0	36	75
propan-2-ol–DMA–water (18:4:3)	47.0	85	85
butan-2-ol–DMF–water (18:4:3)	39.2	47	75
butan-2-ol–DMA–water (18:4:3)	39.2	95	85
1-phenylethanol–dioxane–water (10:12:3)	16.6	58	90
benzyl alcohol–dioxane–water (10:12:3)	19.3	52	90
cyclohexanol–toluene[d]–dioxane–water (10:2:10:3)	19.2	33	90
benzhydrol–dioxane–water (6:22:3)	6.5	25	90
2-methoxyethanol–toluene[d]–water (17:5:3)	43.1	34	65
tetrahydrofurfuryl alcohol–toluene[d]–water (17:5:3)	35.1	45	65

[a][Glucose]: 0.2 M; $[RuCl_2(PPh_3)_3]$: 1.67×10^{-3} M; [Glucose]/$[RuCl_2(PPh_3)_3]$: 120; temp: 100 °C; time 10 h.

[b]Percent selectivity to sorbitol. The other product is glucono-1,5-lactone.

[c]The numbers in parentheses give volume in millilitres of the solvents, except benzhydrol which is expressed in grams.

[d]Added to increase the solubility of the catalyst.



α- & β-D-Glucopyranoses Aldehydo-glucose D-Glucono-1,5-lactone Sorbitol

Scheme 2. Disproportionation of glucose.

visual comparison of the sports on TLC plates to determine the magnitude of this parallel reaction. This was achieved as follows: various known compositions of glucose–sorbitol–glucono-1,5-lactone were prepared and separated using a freshly prepared eluent system which consisted of ethyl acetate–pyridine–water (15:6:1). After developing the TLC spots, the areas and the intensities were compared with that of reaction product. The results are presented in Table 1.

α- and β-D-glucopyranoses are thought to be involved in the above side reaction (disproportionation), meaning that glucose behaves as both hydrogen donor (pyranose forms) and acceptor (aldehyde form) (Scheme 2). Theoretically, any of the five hydroxyl groups (one primary and four secondary) in α- and β-D-glucopyranoses can take part in the reaction. The participation of primary hydroxyl group can be ruled out based on the fact that secondary alcohols are better hydrogen donors than primary alcohols. Among the secondary hydroxyl groups, that forming part of the hemiacetal function (1-

hydroxyl group) is the most active, possibly as a result of the greater acidity of this hydroxyl arising from the inductive effect (–I) of the ring-oxygen atom [24]. Electron density measurements also support this evidence [25]. Hence, it is concluded that the highly active lactol group participates in the redox reaction.

Since both α- and β-D-glucopyranoses yield the same product, namely, D-glucono-1,5-lactone, it is difficult to determine the relative reactivities of the α- and β-forms. We presume that β-D-glucopyranose is a better donor than the α-form, based on the following data. The 1-hydroxyl group in the β-anomer is more acidic than that in the α-anomer [26]. For example, at 25 °C, ionization constants for α- and β-anomers are $K_\alpha = 3.42 \times 10^{-13}$, and $K_\beta = 6.72 \times 10^{-13}$ respectively. Spatial disposition of the anomeric hydroxyl group in β-isomer (equatorial) is favorable for coordination with the Ru(II) complex. In this context, it is emphasized that the α-isomer is more active in the presence of heterogeneous catalysts. It has been proved that α-D-glucopyranose is more easily oxidized than the β-isomer to gluconic acid by Pt because the hydrogen atom geminal to the 1-hydroxyl group is sterically unhindered for adsorption on the metal surface [24].

Transfer hydrogenation by cyclohexanol, benzyl alcohol, 1-phenylethanol and benzhydrol

It is observed from previous results [8] that basic compounds and amide solvents promote disproportionation of glucose. In order to enhance exclusively transfer hydrogenation of glucose, the reactions were carried out using a non-coordination solvent such as dioxane. This solvent was chosen based on its ability to mix with both water and organic solvents (a homogenizing agent) and also its poor hydrogen-donating character [8]. The percent conversions of glucose in the above four hydrogen donors are summarized in Table 1. It was observed that for a certain time interval, only transfer hydrogenation of glucose is detected. This is evidenced from the formation of sorbitol and dehydrogenated products of the hydrogen donors such as acetophenone, benzaldehyde, cyclohexanone and benzophenone, which were identified by gas and thin-layer chromatographies.

Despite using a solvent system devoid of amide solvents, disproportionation of glucoses begins after a definite time lapse. A possible reason could be that the catalyst undergoes very slow deactivation by aldehydo–glucose and the deactivated complex catalyzes only disproportionation. This conclusion is supported by the observation that the catalyst color changes from dark red to light red as the reaction progresses. Such deactivation of the catalysts by carbonylation reactions is reported in the literature. $RuCl_2(PPh_3)_3$ is transformed to $RuCl_2(CO)(PPh_3)_2(DMF)$ and $RuCl_2(CO)(PPh_3)_2(DMA)$ during disproportionation of glucose in DMF and DMA solvents, respectively [27]. Andrews *et al.* [28, 29] have observed that Wilkinson's catalyst undergoes a facile carbonylation to $RhCl(CO)(PPh_3)_2$ in the presence of aldose sugars.

Transfer hydrogenation by 2-methoxyethanol and tetrahydrofurfuryl alcohol

2-Methoxyethanol and tetrahydrofurfuryl alcohol were also chosen as hydrogen donors since they have the additional advantage of dissolving glucose and the catalyst to some extent. The functional group R–O–C–C–O–H present in these two alcohols is responsible for the solubility of monosaccharides. The glucose conversions obtained with these hydrogen donors are shown in Table 1. Unlike other secondary alcohol donors, the initial dark-red color of the reaction solution gradually changes to rose-red and then to yellow (in 90 min) when these alcohols are employed as donors. The color change may be due to carbonylation of the catalyst by these hydrogen donors. This carbonylation is confirmed by the IR spectra of the catalyst isolated from the reaction solution (Fig. 1). From the IR stretching frequency values (ν(RuH) = 2040 cm^{-1} and ν(CO) = 1945 cm^{-1}), it is inferred that the transformed catalyst seems to be a derivative of $RuHCl(CO)(PPh_3)_3$. The ν(RuH) and ν(CO) values reported by different researchers for $RuHCl(CO)(PPh_3)_3$ are (i) 2010 and 1920 cm^{-1} [19], (ii) 2010 and 1918 cm^{-1} [30] and (iii) 2017 and 1924 cm^{-1} [31]. It is seen from Fig. 1 that the frequency values of the crude complex isolated form the reaction solution are slightly shifted towards higher values. This suggests that the electronic environment around Ru(II) is somewhat perturbed due to the replacement of one of the PPh_3 ligands by the dehydrogenated product of the hydrogen donor which absorbs at 1610 cm^{-1}. Moreover, the spatial disposition of the ligands in the isolated complex may not be the same as in crystalline $RuHCl(CO)(PPh_3)_3$.

Analysis of the products from glucose at various time intervals indicated that initial transfer hydrogenation is followed by disproportionation of glucose. As long as $RuCl_2(PPh_3)_3$ is in the reaction solution, only transfer hydrogenation is observed; once it is transformed to the hydridocarbonyl complex, dis-

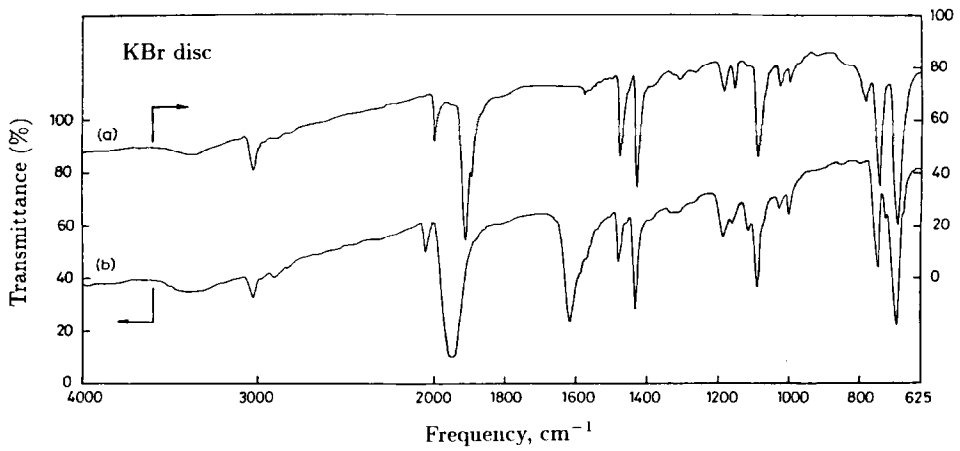


Fig. 1. Infrared spectra of (a) $RuHCl(CO)(PPh_3)_3$ and (b) the catalyst isolated from the reaction medium when tetrahydrofurfuryl alcohol was used as hydrogen donor.

proportionation begins. This clearly shows that the hydridocarbonyl complex is able to catalyze the disproportionation and not the transfer hydrogenation by these alcohols. This has been proved by carrying out the reactions independently with $RuHCl(CO)(PPh_3)_3$ in these alcohols, where disproportionation of glucose is observed from the start [32].

Mechanism of transfer hydrogenation

From the above observations, the following mechanism is proposed for the transfer hydrogenation of glucose:

$$RuCl_2P_3 \rightleftharpoons RuCl_2P_2 + P \quad (1)$$

$$RuCl_2P_2 + R'R''CHOH \rightleftharpoons RuClP_2(R'R''CHO) + HCl \quad (2)$$

$$RuClP_2(R'R''CHO) \rightleftharpoons RuHClP_2(R'R''CO) \quad (3)$$

$$RuHClP_2(R'R''CO) + RCHO \rightleftharpoons RuHClP_2(R'R''CO)(RCHO) \quad (4)$$

$$RuHClP_2(R'R''CO)(RCHO) \rightleftharpoons RuClP_2(R'R''CO)(RCH_2O) \quad (5)$$

$$RuClP_2(R'R''CO)(RCH_2O) + HCl \rightleftharpoons RuCl_2P_2(R'R''CO) + RCH_2OH \quad (6)$$

$$RuCl_2P_2(R'R''CO) \rightleftharpoons RuCl_2P_2 + R'R''CO \quad (7)$$

where P = triphenylphosphine, RCHO = aldehyde form of glucose and R'R"CHOH = primary (R" = H) or secondary alcohol.

In the case of 2-methoxyethanol and tetrahydrofurfuryl alcohol, the dehydrogenated product, R'CHO ($R' = CH_3OCH_2-$ or tetrahydrofurfuryl) may compete with the aldehyde form of glucose (RCHO) at stage (4) to form $RuHClP_2(R'CHO)_2$. This compound is transformed to hydridocarbonyl complex via an unstable isocarbonyl complex [33]:

$$RuHClP_2(O{=}CHR')(R'CHO) \longrightarrow$$

$$[RuHClP_2(OC)(R'CHO)] \longrightarrow RuHClP_2(CO)(R'CHO) \quad (8)$$

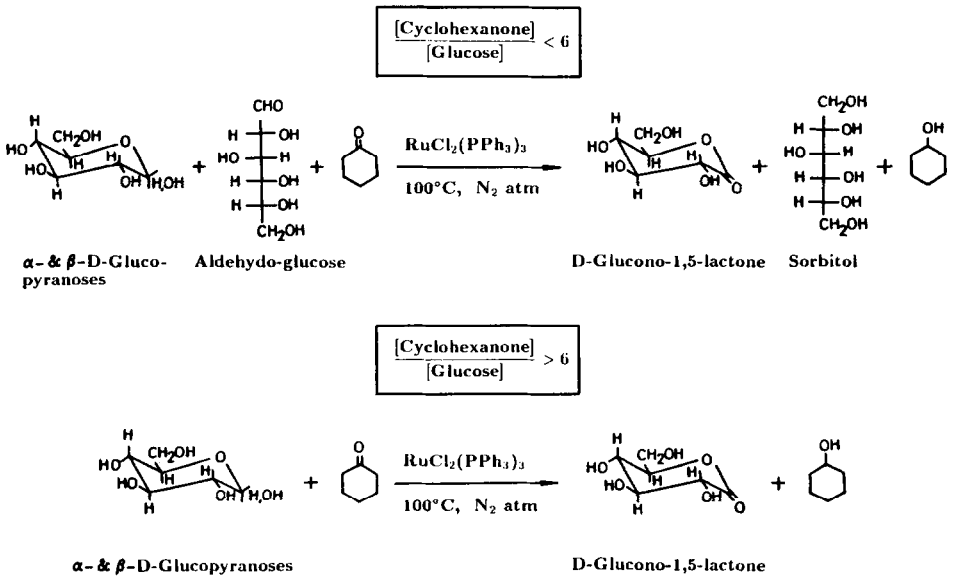
All our attempts to detect the dehydrogenated and decarbonylated products, CH_3OCH_2CHO, CH_3OCH_3, tetrahydrofurfural and tetrahydrofuran were unsuccessful. This is attributed to their low concentrations.

Transfer hydrogenation of cyclohexanone by glucose

The fact that glucose disproportionates to yield sorbitol and glucono-1,5-lactone, even in the presence of other hydrogen donors, indicates that glucopyranoses are good hydrogen donors. This property offers a potentially convenient procedure for transfer hydrogenation of various functional groups using glucose as hydrogen donor.

In the present study, cyclohexanone was transfer hydrogenated under homogeneous conditions by glucose. For this reaction, tetrahydrofurfuryl alcohol was chosen as solvent and $RuCl_2(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, $RuH_2(PPh_3)_4$ and $RuH_2(CO)(PPh_3)_3$ as catalysts. In the case of $RuCl_2(PPh_3)_3$, the effective catalyst may be $RuHCl(CO)(PPh_3)_3$ since the former is transformed to the latter in this solvent. Such transformation is completed in 15 min

when the solvent system consists of 22 parts tetrahydrofurfuryl alcohol and 3 parts water. At a molar ratio of 1:2 of glucose and cyclohexanone, the products obtained are cyclohexanol, sorbitol and glucono-1,5-lactone (Scheme 3). It is deduced from this observation that both cyclohexanone and the aldehyde form of glucose compete for coordination sites. As the concentration of cyclohexanone increases, the amount of sorbitol formed decreases. At molar ratios of 1:6 and above, only cyclohexanol is observed as the reduction product (Scheme 3), *i.e.*, at high concentrations of cyclohexanone, the aldehyde



Scheme 3. Transfer hydrogenation of cyclohexanone by glucose.

TABLE 2

Transfer hydrogenation of cyclohexanone by glucose[a]

[Cyclohexanone] / [Glucose]	Glucose conversion (%)	Cyclohexanone conversion (%)	S:GL[b]
2.0	83	[c]	35:65
4.0	77	[c]	20:80
6.0	76	12	0:100
8.0	78	[c]	0:100

[a]Solvent: tetrahydrofurfuryl alcohol–water (22:3); [Glucose]: 0.2 M; $[RuCl_2(PPh_3)_3]$: 1.67×10^{-3} M; [Glucose]/$[RuCl_2(PPh_3)_3]$ ratio: 120; temp: 100 °C; time: 10 h.
[b]S:GL denotes sorbitol:glucono-1,5-lactone ratio.
[c]Estimation was not made.

form of glucose in the solution becomes insignificant and hence sorbitol is not formed. The results are provided in Table 2.

It is relevant to show that tetrahydrofurfuryl alcohol is not involved in the transfer hydrogenation of cyclohexanone under these conditions. This has been confirmed by estimating the cyclohexanol and glucose by GC and titrimetry respectively. It was found that equivalent amounts of glucose and cyclohexanone are transformed into glucono-1,5-lactone and cyclohexanol respectively. Also, an independent experiment with cyclohexanone in the above solvent yielded no significant reaction. However, at reflux temperatures, tetrahydrofurfuryl alcohol reduced cyclohexanone in the presence of the above-mentioned ruthenium complexes.

Conclusions

Glucose was transfer hydrogenated by various hydrogen donors under the catalytic influence of $RuCl_2(PPh_3)_3$. The major product of the reaction was sorbitol, albeit a side product, glucono-1,5-lactone, is formed as the reaction proceeds as a result of the disproportionation of glucose. The catalyst undergoes a permanent change by abstracting CO from the dehydrogenated product of 2-methoxyethanol or tetrahydrofurfuryl alcohol. The resultant catalyst was isolated and characterized to be $RuHCl(CO)(PPh_3)_3$.

At low concentration ratio of cyclohexanone to glucose, α- and β-glucopyranoses donate hydrogens to aldehydo–glucose and cyclohexanone. When the molar ratio of cyclohexanone to glucose exceeds 6, aldehydo-glucose fails to participate in the reaction. As a result, cyclohexanone is reduced to cyclohexanol and glucose is oxidized to glucono-1,5-lactone.

It should be mentioned here that the results presented in this article are of little practical value*.

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References

1 R. A. W. Johnstone, A. H. Wilby and I. N. Entwistle, *Chem. Rev.*, *85* (1985) 129.
2 G. Brieger and T. J. Nestrick, *Chem. Rev.*, *74* (1974) 567.
3 I. S. Kolomnikov, V. P. Kukolev and M. E. Vol'pin, *Russ. Chem. Rev.*, *43* (1974) 399.
4 K. Ashida, *J. Agric. Chem. Soc. Jpn.*, *20* (1944) 621.
5 K. Ashida, *J. Agric. Chem. Soc. Jpn.*, *23* (1949) 167; (1949) 170; (1949) 174.
6 *Jap. Pat. 172 087* (1946) to B. Suzuki and A. Ashida.

*This sentence was included upon the recommendation of one of the referees.

7 J. V. Karbinos and A. I. Ballum, *J. Am. Chem. Soc., 75* (1953) 4501.
8 S. Rajagopal, S. Vancheesan, J. Rajaram and J. C. Kuriacose, *Proc. 4th Natl. Sym. on Catal.*, Bombay, 1978, p. 380.
9 S. Rajagopal, S. Vancheesan, J. Rajaram and J. C. Kuriacose, *Indian J. Chem., 18B* (1979) 293.
10 M. Delepine and A. Horeau, *Bull. Soc. Chim. Fr., 4* (1937) 1524.
11 K. Ashida, S. Nakamura and T. Beboko, *J. Agric. Chem. Soc. Jpn., 23* (1950) 231.
12 M. Nakazaki, *J. Chem. Soc. Jpn., Pure Chem. Sect., 75* (1954) 831.
13 G. de Wit, J. J. de Vlieger, A. C. Kock-van Dalen, A. P. G. Kieboom and H. van Bekkum, *Tetrahedron Lett.*, (1978) 1327.
14 A. J. van Hengstum, A. P. G. Kieboom and H. van Bekkum, *Starch/Staerke, 36* (1984) 317.
15 G. Descotes and D. Sinou, *Tetrahedron Lett.*, (1976) 4083.
16 G. Descotes, J. Sabadie and D. Sinou, *Tetrahedron Lett.*, (1978) 3351.
17 G. Descotes, J. P. Praly and D. Sinou, *J. Mol. Catal., 6* (1979) 421.
18 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28* (1966) 945.
19 J. J. Levison and S. D. Robinson, *J. Chem. Soc., A*, (1970) 2947.
20 N. Ahmad, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, (1972) 843.
21 A. I. Vogel, *Textbook of Practical Organic Chemistry, 3rd ed.*, ELBS Longmans, London, 1971.
22 A. I. Vogel, *Elementary Practical Organic Chemistry, Part III. Quantitative Organic Analysis*, ELBS Longmans, London, 1975, p. 745.
23 S. R. Maple and A. Allerhand, *J. Am. Chem. Soc., 109* (1987) 3168.
24 A. H. Haines, in R. S. Tipson and D. Horton (eds.), *Adv. Carbohydr. Chem. Biochem., 33* (1976) 11.
25 Yu. A. Zhdanov, V. I. Minkin, Yu. A. Ostroumov and G. N. Dorofeenko, *Carbohydr. Res., 7* (1968) 156.
26 H. S. Isbell and W. Pigman, in M. L. Wolfrom and R. S. Tipson (eds.), *Adv. Carbohydr. Chem. Biochem., 24* (1969) 13.
27 S. Rajagopal, S. Vancheesan, J. Rajaram and J. C. Kuriacose, *J. Mol. Catal., 22* (1983) 131.
28 M. A. Andrews and S. A. Klaeren, *J. Chem. Soc., Chem. Commun.*, (1988) 1266.
29 M. A. Andrews, G. L. Gould and S. A. Klaeren, *J. Org. Chem., 54* (1989) 5257.
30 R. K. Poddar and U. Agarwal, *Indian J. Chem., 9* (1971) 477.
31 J. Chatt and B. L. Shaw, *Chem. Ind.*, (1961) 290.
32 S. Rajagopal, S. Vancheesan, J. Rajaram and J. C. Kuriacose, *J. Mol. Catal., 22* (1983) 137.
33 J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.*, (1964) 3466.