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THE MECHANISM OF DISPROPORTIONATION OF D-GLUCOSE CATALYSED BY HYDRIDOCHLOROCARBONYLTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) IN TETRAHYDROFURFURYL ALCOHOL

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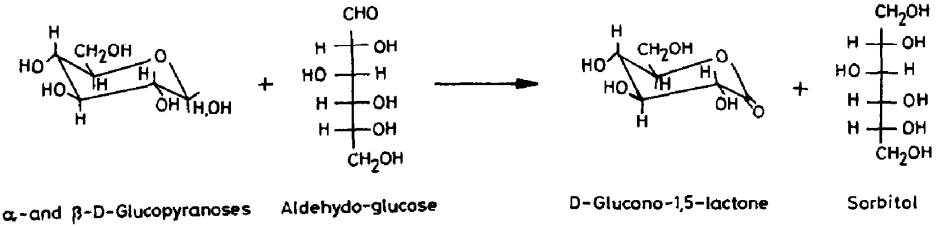
Summary

The disproportionation of D-glucose in tetrahydrofurfuryl alcohol (THFA) catalysed by $RuHCl(CO)(PPh_3)_3$ is suggested to proceed by hydride transfer from a dissociated catalyst species to the coordinated aldehyde form of glucose. Subsequent steps involve the coordination of the pyranose form of glucose, formation of the metal alkoxide, release of D-glucitol and hydrogen transfer from alkoxide to the metal. The kinetic data are compatible with the rate expression, rate = $(kK[G][Ru]_0)/([P] + K)$, where k, K, $[G]$, $[Ru]_0$ and $[P]$ represent the rate constant of the rate-determining step, the equilibrium constant for the dissociation of the catalyst, concentrations of glucose, catalyst and added triphenylphosphine respectively.

Introduction

The transfer hydrogenation of D-glucose at 100 °C catalysed by $RuCl_2(PPh_3)_3$ is also accompanied by disproportionation of D-glucose [1, 2]. The extent of the disproportionation reaction is less in secondary alcohols such



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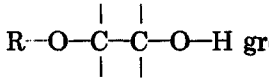
as 1-phenylethanol. But in 2-methoxyethanol or THFA, the catalyst is converted into a hydridochlorocarbonyl complex, $RuHCl(CO)(PPh_3)_3$ [3, 4], if there is an accumulation of sufficient dehydrogenated product of the hydrogen donor. This carbonyl complex catalyses only the disproportionation of glucose, and thus the disproportionation reaction predominates in these solvents. A detailed investigation of the disproportionation of glucose in THFA catalysed by $RuHCl(CO)(PPh_3)_3$ was therefore undertaken.

Results and discussion

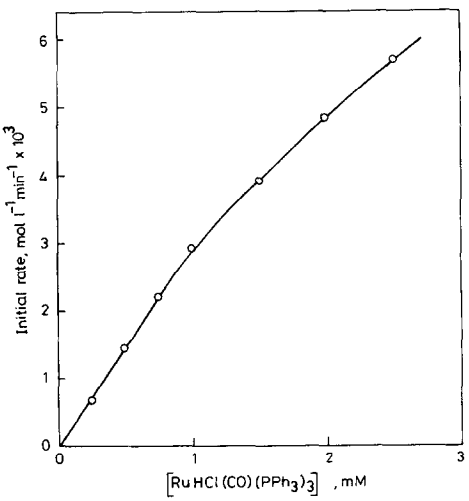
Tetrahydrofurfuryl alcohol is used as a solvent since the



group facilitates the solubility of glucose through hydrogen bonding [5]. It is observed that the title complex is a very poor catalyst for the transfer hydrogenation of glucose by tetrahydrofurfuryl alcohol.

Dependence on the catalyst concentration

When less than 1 mM of $RuHCl(CO)(PPh_3)_3$ is used at 110 °C, the initial rate of disproportionation of glucose is linearly related to the concentration of the catalyst (Fig. 1). In this region, the dissociation of the catalyst into the active catalytic species $RuHCl(CO)(PPh_3)_2$ and PPh_3 may be almost



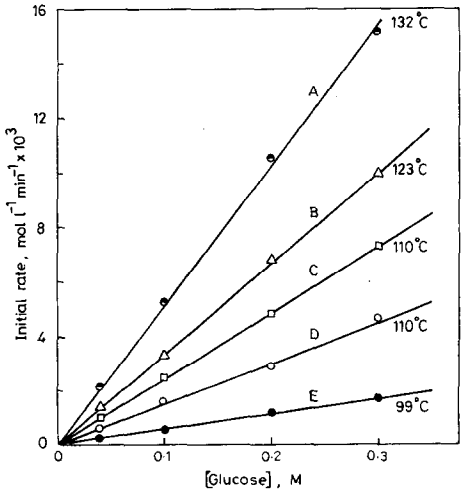


Fig. 1. Plot of initial rate *vs.* concentration of the catalyst indicating first order with respect to the catalyst. Reaction conditions: [glucose] = 0.2 M; $[RuHCl(CO)(PPh_3)_3]$ = 0.25 - 2.50 mM; solvent = THFA; temperature = 110 °C.

Fig. 2. Dependence of initial rates on concentrations of glucose at various temperatures. Reaction conditions A, B, D and E, $[RuHCl(CO)(PPh_3)_3]$ = 1 mM; C, $[RuHCl(CO)(PPh_3)_3]$ = 2 mM.

complete, and the reaction is first order with respect to the catalyst. However, at higher catalyst concentrations (>1 mM), a deviation is observed which may be attributed to the nonavailability of all the catalyst for the reaction as a result of dimerization [6, 7]. Dimerization in the case of Wilkinson's catalyst has been reported [8].

Dependence on the glucose concentration

Plots of initial rate against the concentration of glucose (0.04 - 0.3 M) are linear (Fig. 2), establishing a first-order dependence on the concentration of glucose. This indicates that the coordination of glucose, either in the acyclic or pyranose form (probably the former which is likely to be a better coordinating ligand), might be the rate-determining step. The order in glucose is one, even at higher concentrations of the catalyst (Fig. 2C).

Solvents

The catalyst is soluble in solvents of high polarity and strong coordinating ability, such as DMF and DMA, but the reaction does not proceed as fast as in tetrahydrofurfuryl alcohol (Table 1), probably due to the nonavailability of coordination sites which are blocked by these solvent molecules.

From the infrared spectrum of the complex isolated from the reaction mixture and that of $RuHCl(CO)(PPh_3)_3$ (Fig. 3), it is seen that the stretching frequencies of both Ru—H and CO are shifted towards the high-energy region. This can be attributed to a decrease in electron density on ruthenium as a result of the replacement of phosphine, which is a Lewis base donor, by the substrate or solvent molecule which has a strong tendency to accept electrons from the metal. This reduces M→CO back donation and the bond order, leading to an increase in ν_{CO}.

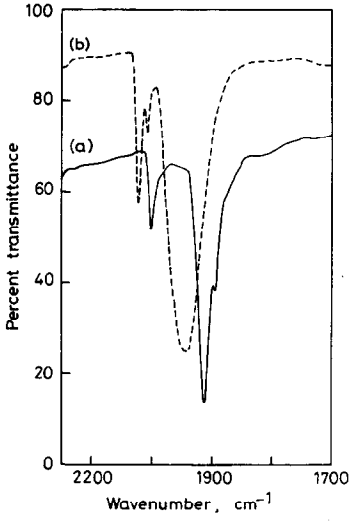
To find the extent of formation of the acyclic form of glucose (hydrogen acceptor) in tetrahydrofurfuryl alcohol, measurement of optical rotation was made at 589 nm. The value of 52° for the specific rotation indicates that the aldehyde form of glucose is in equilibrium with glucopyranoses under the reaction conditions. Since the rate is proportional to the concentration of the catalyst, it is clear that the rate of mutarotation of glucose is faster than the disproportionation of glucose.

TABLE 1

Effect of solvents on disproportionation of glucose

Serial No.	[Glucose] (M)	[$RuHCl(CO)(PPh_3)_3$] (mM)	Solvent	Initial rate × 10^3 (mol l^{-1} min^{-1})
1	0.2	5	DMF	0.89
2	0.2	5	DMA	4.57
3	0.2	1	THFA	6.82

Temperature 123 °C.



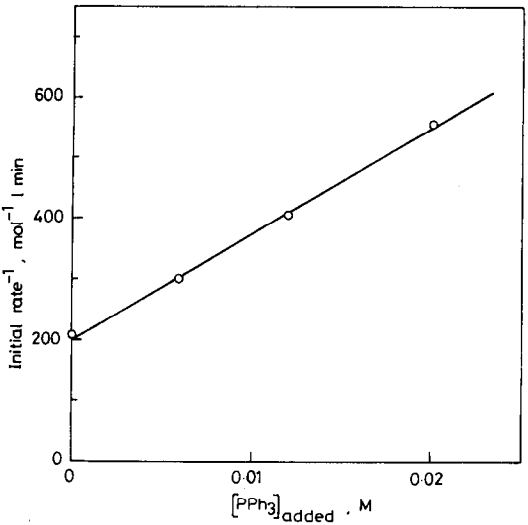


Fig. 3. IR spectra (KBr disc) of (a) $RuHCl(CO)(PPh_3)_3$ (authentic sample) and (b) the catalyst after the reaction between glucose and $RuHCl(CO)(PPh_3)_3$ in THFA.

Fig. 4. Dependence of initial rate of disproportionation of glucose on the concentration of triphenylphosphine added to the system. Reaction conditions: [glucose] = 0.3 M; $[RuHCl(CO)(PPh_3)_3]$ = 2 mM; solvent = THFA; temperature = 110 °C.

Effect of added triphenylphosphine

The rate of disproportionation of glucose is decreased by the addition of excess triphenylphosphine (P) to the reaction system, as observed in the case of hydrogen transfer [9 - 11] and reduction with molecular hydrogen [12 - 14]. This might be due to the effect of excess triphenylphosphine on the dissociation of $RuHCl(CO)(PPh_3)_3$. The reciprocal of the rate shows a linear dependence on the concentration of added triphenylphosphine (Fig. 4). The linear dependence can thus be expressed in the form $1/\text{rate} = a + b[PPh_3]_{added}$, where a and b are constants. From Fig. 4, $a = 200$ mol^{-1} min and $b = 1.8 \times 10^4$ mol^{-2} l^2 min. From these values the equilibrium constant for the dissociation of the catalyst can be calculated.

From the kinetic data and the examples cited in the literature [10, 15 - 19], the process of disproportionation of glucose may be represented as follows:

$$RuHCl(CO)P_3 \overset{K}{\rightleftharpoons} RuHCl(CO)P_2 + P$$

$$RuHCl(CO)P_2 + G \xrightarrow[(slow)]{k} \text{products}$$

Here the coordination of the acyclic form of glucose (G) is considered as the rate-determining step. Subsequent fast steps are hydride transfer to G, coordination of LH_2 (α or β-D-glucopyranose) and formation of the products sorbitol and glucono-1,5-lactone (L). The disproportionation reaction is

quantitative, and as the product L is an internal ester (lactone) it is less likely to coordinate with the catalyst.

Based on this reaction scheme, the rate (R) can be expressed as:

$$R = \frac{kK[G][Ru]_0}{[P] + K} \quad (1)$$

where K and k are the equilibrium and rate constants respectively and [G], $[Ru]_0$ and [P] are the concentrations of glucose, catalyst and triphenylphosphine respectively.

At low concentrations of the catalyst (<1 mM) the concentration of triphenylphosphine is small when compared to K, and hence the rate expression reduces to:

$$R = k[G][Ru]_0 \quad (2)$$

Equation (2) accounts for the experimental observations. The values of k obtained from plots of rate against [catalyst] and rate against [glucose] are 14.7 l mol^{-1} min^{-1} and 15.0 l mol^{-1} min^{-1} respectively.

At high concentrations of the catalyst (>1 mM), [P] is not negligible compared to K and hence eqn. (1) is the rate expression to be used. The concentration of the added triphenylphosphine is so large that the concentration of triphenylphosphine derived from the dissociation of the catalyst may be neglected. Thus $[P] \simeq [P]_{added}$. Equation (1) can be rearranged to give eqn. (3):

$$\frac{1}{R} = \frac{1}{kK[G][Ru]_0}[P] + \frac{1}{k[G][Ru]_0} \quad (3)$$

This accounts for the observed linear relationship between $1/R$ and $[P]_{added}$. From the slope and intercept of this plot, k and K are calculated to be 12.5 mol^{-1} l min^{-1} and 1.14 mol l^{-1} respectively.

Dependence on temperature

Initial rates were measured at 132, 123, 110 and 99 °C for four different concentrations of glucose (0.04 - 0.3 M) keeping the concentration of the catalyst at 1 mM in each case. The order with respect to glucose remains unchanged at these temperatures. From the initial rate values, the second-order rate constant k is calculated using the rate expression $R = k[G][Ru]_0$. First-order plots are also made for different initial concentrations of glucose for each temperature, and the values of k_{obs} are obtained.

From the Arrhenius plot of log k against T^{-1} (Fig. 5A) the activation energy, E_a is found to be 79.1 kJ mol^{-1}, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are calculated to be 75.8 kJ mol^{-1} and −60.7 J mol^{-1} respectively.

Dependence of equilibrium constant on temperature

Studies on the inhibition of the disproportionation of glucose by triphenylphosphine were made at four temperatures. From the plots of (initial rate)$^{-1}$ against $[PPh_3]_{added}$, the equilibrium constant K is calculated (Table 2).

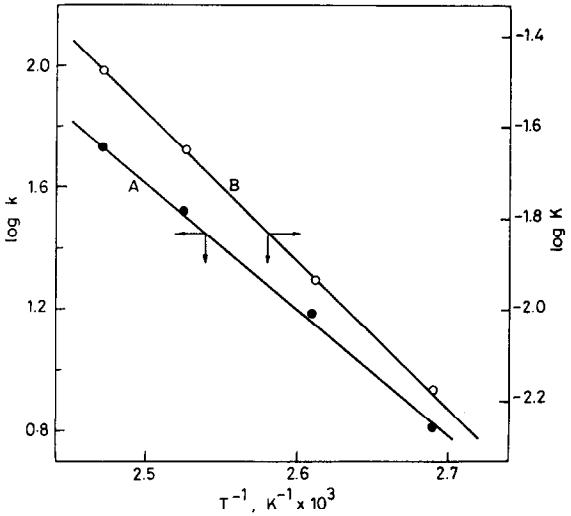


Fig. 5. Plots of (A) log (rate constant) against $1/T$ to determine the energy of activation and (B) log (equilibrium constant) against $1/T$ to determine the enthalpy of dissociation of $RuHCl(CO)(PPh_3)_3$.

TABLE 2

Equilibrium constants for the dissociation of $RuHCl(CO)(PPh_3)_3$ at four temperatures

Serial No.	Temperature (°C)	K (mol l^{-1} x 10^2)
1	132	3.05
2	123	2.22
3	110	1.14
4	99	0.65

From the plot of log K *vs.* T^{-1} (Fig. 5B) the enthalpy change (ΔH^0) accompanying the dissociation of $RuHCl(CO)(PPh_3)_3$ has been calculated to be 62.0 kJ mol^{-1}.

Experimental

Materials

Hydridochlorocarbonyltris(triphenylphosphine)ruthenium(II) was prepared by the literature method [20]. Tetrahydrofurfuryl alcohol (BDH) was purified by distillation. $RuCl_3 \cdot xH_2O$ (Johnson Matthey) and anhydrous α-D-glucose (Pfizer) were used as such. Triphenylphosphine (Ventron Corp) was recrystallised from a mixture of benzene and methanol.

Kinetic studies

The substrate and deaerated solvent were placed in the inner portion of an all-glass double-walled apparatus with provision for heating by vapours of a liquid circulating in the annular space, mechanical stirring, temperature measurement, passing an inert gas and withdrawing aliquots of the reaction mixture. The progress of the reaction was followed by volumetric determination of the concentration of unreacted glucose [21] at various time intervals.

IR study

The reaction mixture containing the catalyst and the products was evaporated under reduced pressure and the resulting solution diluted with water. It was then boiled for about 5 min in the presence of small amounts of sodium chloride. The yellow complex which precipitated was filtered and washed thoroughly with water to remove sodium chloride, glucose and other soluble materials. The IR spectrum of the dry complex was recorded on a Perkin-Elmer 257 spectrophotometer (KBr disc).

Measurement of optical rotation

α-D-glucose (0.9 g) was heated in tetrahydrofurfuryl alcohol (25 ml) to 110 °C with constant stirring. After complete dissolution it was heated further for 15 min and cooled immediately to room temperature. Optical rotation of the solution was measured at 27 °C and at a wavelength of 589 nm using a Pye-Unicam spectropolarimeter.

Measurement of initial rate

The initial rate was measured as the slope of the initial portion of the concentration–time plot (Fig. 6) if it is linear, or by the mirror method [22] in other cases.

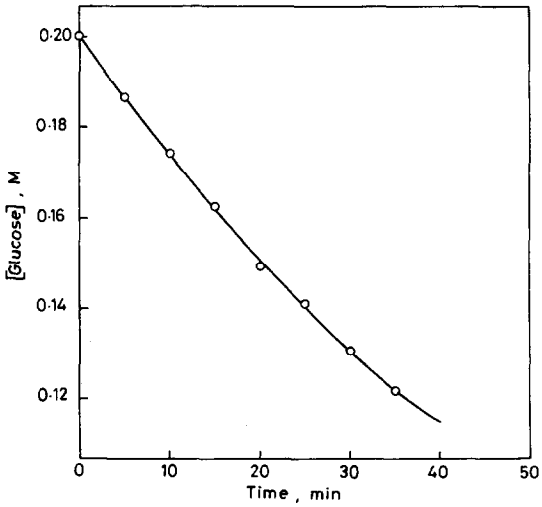


Fig. 6. Concentration–time plot for the disproportionation of glucose in THFA catalysed by $RuHCl(CO)(PPh_3)_3$. Reaction conditions: [glucose] = 0.2 M; $[RuHCl(CO)(PPh_3)_3]$ = 1 mM; solvent = THFA; temperature = 110 °C.

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