DEACTIVATION OF $RuCl_2(PPh_3)_3$ DURING DISPROPORTIONATION OF D-GLUCOSE IN AMIDE SOLVENTS

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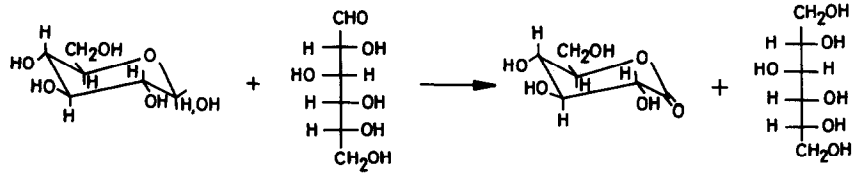
Summary

The catalyst $RuCl_2(PPh_3)_3$ is transformed into a catalytically inactive complex $RuCl_2(CO)(PPh_3)_2(DMF)$ during disproportionation of D-glucose in dimethylformamide (DMF). In dimethylacetamide (DMA), the catalyst is converted to $RuCl_2(CO)(PPh_3)_2(DMA)$ and *cis*-$RuCl_2(CO)_2(PPh_3)_2$. The aldehydo-glucose is shown to be the main source of carbon monoxide.

Introduction

Reactions of different classes of organic compounds catalysed by transtion metal complexes are well documented [1, 2]. However, only a few examples relate to the hydrogenation [3 - 6], transfer hydrogenation [5, 7] and disproportionation [5, 7, 8] of monosaccharides (mainly glucose). Glucose has been used as a hydrogen donor for unsaturated fatty acid esters [9], cyclohexanone [7] and α,β-unsaturated carbonyl compounds [8].

During our investigation [5, 7] of the hydrogenation and transfer hydrogenation of glucose catalysed by $RuCl_2(PPh_3)_3$, glucose was found to undergo a redox reaction (eqn. 1) in solvents such as dimethylformamide (DMF) and dimethylacetamide (DMA). To understand the mechanism of



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$RuCl_2(PPh_3)_3$-catalysed disproportionation of glucose in amide solvents, a systematic kinetic study was undertaken. During the reaction, the catalyst was found to be deactivated by a decarbonylation reaction. The isolation and characterisation of the inactive intermediates are reported in this paper.

Experimental

$RuCl_2(PPh_3)_3$ [10], $RuCl_2(CO)(PPh_3)_2(DMF)$, $RuCl_2(CO)(PPh_3)_2(DMA)$ and *cis*-$RuCl_2(CO)_2(PPh_3)_2$ [11] are prepared by methods reported in the literature. The disproportionation reactions of glucose are carried out in a double-walled cylindrical vessel with provisions for heating the reaction mixture by the vapours of suitable solvents and for maintaining an inert atmosphere. The catalytic intermediates are separated by distilling off the solvent under vacuum followed by the addition of warm water and sodium chloride. They are then filtered, washed with water followed by ether, and dried under vacuum at 50 °C. The quantity of the catalytic intermediate $RuCl_2(CO)(PPh_3)_2(DMF)$ is estimated by taking the IR spectrum of the complex in CH_2Cl_2 and measuring the area under the peak at 1945 cm^{-1}. IR spectra were taken on Perkin-Elmer 257 and Beckman IR 12 instruments. ^1H NMR spectra were recorded on a 100 MHz XL-100 Varian NMR spectrometer.

Results and discussion

Disproportionation of glucose in dimethylformamide

During the disproportionation of glucose in DMF, the reddish-brown colour of the $RuCl_2(PPh_3)_3$ complex changes to yellow. This colour change and the drastic fall in rate after about 35% of glucose had reacted suggest the formation of a catalytically less active species. This species has been isolated and characterised as $RuCl_2(CO)(PPh_3)_2(DMF)$.

Characterisation of $RuCl_2(CO)(PPh_3)_2(DMF)$

The IR spectrum of the sample in a Nujol mull exhibited bands at 1910(s) and 1865(vw) cm^{-1} which can be assigned to carbonyl stretching. A strong band at 1625 cm^{-1} is attributed to the CO stretching frequency of coordinated DMF. The far IR spectrum of the compound exhibited a band at 332 cm^{-1} which is due to *trans*-dichloride (ν(Ru—Cl)). The ^1H NMR spectrum of the compound in $CDCl_3$ with TMS as the internal standard shows two multiplets centered at 7.76 and 7.3 δ and three singlets at 8.01, 3.01 and 2.9 δ. The multiplets are attributed to triphenylphosphine and the three singlets to coordinated DMF. The area under the peaks corresponds to two triphenylphosphine ligands and one DMF molecule per molecule of the complex. The identity of the complex is further confirmed by comparing its IR spectrum with that of an authentic sample of $RuCl_2(CO)(PPh_3)_2(DMF)$ prepared as reported by James *et al.* [11].

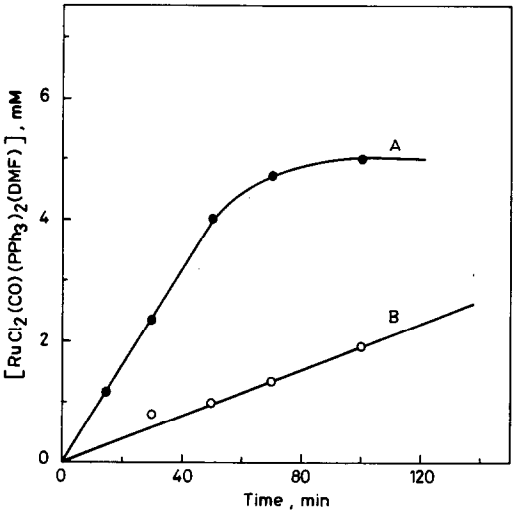

Fig. 1. Plot of concentration of $RuCl_2(CO)(PPh_3)_2(DMF)$ formed *vs.* reaction time. Reaction conditions: (A) [glucose] = 0.2 M, $[RuCl_2(PPh_3)_3]$ = 5 mM, solvent = DMF; temperature 123 °C; (B) $RuCl_2(PPh_3)_3$ = 5 mM, solvent = DMF, temperature 123 °C.

Quantitative estimation of $RuCl_2(CO)(PPh_3)_2(DMF)$

The extent of carbonylation of the catalyst $RuCl_2(PPh_3)_3$ was studied by isolating the complex at different time intervals and estimating by IR spectroscopy. The plot of concentration against time shows that the catalyst is completely converted into $RuCl_2(CO(PPh_3)_2(DMF)$ in 100 min (Fig. 1A). A solution of $RuCl_2(PPh_3)_3$ in DMF which had been heated under nitrogen atmosphere at 123 °C for 100 min also yielded a carbonyl complex (conv. 38%) (Fig. 1B) which is formed via decarbonylation of the solvent [12]. These results indicate that the catalyst is carbonylated mainly by glucose.

Disproportionation of glucose in dimethylacetamide:

The catalyst is also carbonylated and rendered inactive during disproportionation of glucose in DMA. The inactive carbonyl species was found to be a mixture of two complexes. These complexes were separated and purified by crystallisation using a mixture of CH_2Cl_2 and methanol, and then characterised by IR and ^1H NMR spectral studies.

The ^1H NMR spectrum of the first component showed three peaks: one multiplet (6.9 - 7.7 δ) due to phenyl rings and two singlets at 2.95 and 2.1 δ. The areas under the peaks were in the ratio of 10:2:1. Unlike the coordinated DMF in $RuCl_2(CO)(PPh_3)_2(DMF)$, where three singlets appeared (one due to formyl hydrogen and two due to the *N*-methyl groups), coordinated DMA showed only two peaks (Fig. 2(a)). However, the ^1H NMR spectrum of DMA in $CDCl_3$ showed three signals as expected (Fig. 2(b)). The appearance of one signal for the $-N(CH_3)_2$ group can be explained as follows. DMA loses its C=N character on coordination; thereby the two *N*-methyl groups become

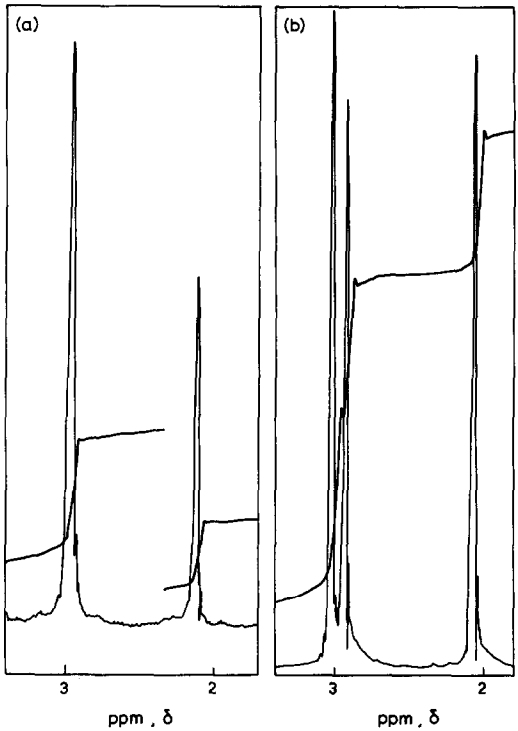

Fig. 2. ^{1}H NMR spectra of (a) DMA in the complex $RuCl_2(CO)(PPh_3)_2$(DMA) and (b) DMA (authentic sample).

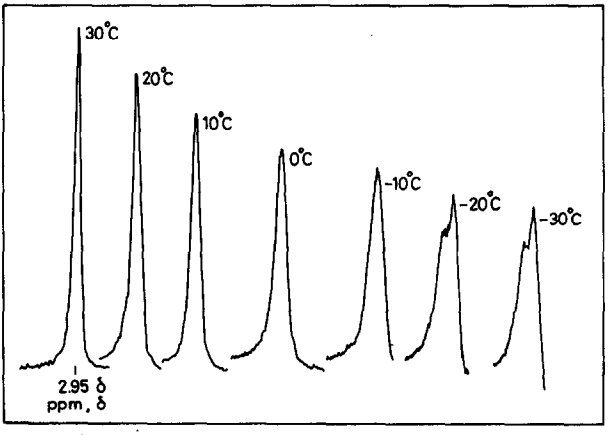

Fig. 3. ^{1}H NMR spectra in $CDCl_3$ of $-N(CH_3)_2$ group of DMA in $RuCl_2(CO)(PPh_3)_2$(DMA) at various temperatures.

magnetically equivalent because of the possibility of free rotation around the C—N bond. Variable-temperature ^{1}H NMR study of the above complex in $CDCl_3$ was undertaken, and it was observed that at −20 °C the singlet of the $-N(CH)_3)_2$ group could be resolved into two peaks (Fig. 3). Using NMR,

IR [ν(C≡O) = 1920 cm^{-1}] and far IR [ν(Ru—Cl) = 325 cm^{-1}] the first component is identified as $RuCl_2(CO)(PPh_3)_2$(DMA).

The second component is a dicarbonyl complex, *viz. cis*-$RuCl_2(CO)_2(PPh_3)_2$ (ν(C≡O): 2040 and 1965 cm^{-1} (lit: 2042 and 1967 cm^{-1} [11])).

In DMA, the two carbonyl complexes can be formed in two ways: (i) they can be formed simultaneously or (ii) the monocarbonyl can be a precursor to the dicarbonyl. To ascertain this, the catalyst was isolated at the end of 50, 100 and 150 min and the IR spectra were recorded. The relative intensity of peaks corresponding to the dicarbonyl complex (2040 and 1965 cm^{-1}) increases, while that corresponding to the monocarbonyl complex (1920 cm^{-1}) decreases with an increase in time thus, showing that the monocarbonyl complex is a precursor to the dicarbonyl complex.

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