

HOMOGENEOUS HYDROGENATION OF KETONES TO ALCOHOLS WITH RUTHENIUM COMPLEX CATALYSTS *

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Summary

A number of ruthenium triphenylphosphine complexes catalyse the reduction of ketones to their corresponding alcohols in the presence of water. The most convenient catalyst precursors are carbonyl containing complexes which do not promote decarbonylation of the substrate. The hydrogenation of acetone with hydridochlorocarbonyltris(triphenylphosphine)ruthenium is first order with respect to the substrate concentration, the catalyst concentration, the hydrogen pressure and the water concentration. Turnover numbers up to 15,000 have been achieved with this catalyst. Other ketones are also reduced by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and the rate of the reaction is dependent on the nature of the substrate.

Introduction

Although several examples of the homogeneous hydrogenation of ketones to alcohols with cobalt [2,3] and rhodium [4–17] complexes have been described, very few ruthenium compounds are known to catalyse this reaction.

Frediani et al. reported the hydrogenation of cyclohexanone using ruthenium hydrido-carbonyl clusters [18,19] whilst Botteghi et al. described the enantioselective reduction of ketones with $\text{H}_4\text{Ru}_4(\text{CO})_8[(-)\text{-DIOP}]_2$ [20]. At the outset of this work the only mononuclear ruthenium complexes which had been mentioned as catalysts for the reduction of ketones were $\text{RuCl}_2(\text{PPh}_3)_3$ [21] and $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$ [22]; while our investigations were in progress Strohmeier and Weigelt reported the use of $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ as homogeneous catalysts for the hydrogenation of ketones [23].

* Preliminary communication, ref. 1.

We have now studied the catalytic activity of a series of ruthenium compounds using as a model reaction the reduction of acetone to isopropanol in the absence of solvent. The most convenient catalyst precursor is hydrido-chlorocarbonyltris(triphenylphosphine)ruthenium, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, and a detailed study of the factors affecting the activity and selectivity of this complex in this reaction has been carried out. Kinetic measurements under appropriate reaction conditions are reported.

Results and discussion

The catalysts

Results of the hydrogenation of acetone with several ruthenium complexes at 150°C and 68 atm H_2 are shown in Table 1. Under these conditions all the mononuclear complexes studied are more active than the cluster $\text{Ru}_3(\text{CO})_{12}$. The highest activity and selectivity were obtained with those catalysts containing carbonyl or nitrosyl ligands; this is due to the fact that for complexes of general formula $\text{RuX}_2(\text{PPh}_3)_n$, [$\text{X} = \text{H}, \text{Cl}; n = 3, 4$] decarbonylation of the ketone competes with the hydrogenation reaction, as evidenced by the isolation of metal carbonyl complexes after the reaction has been completed.

Addition of water generally causes a marked increase in the reaction rate, in accord with previous reports using cationic rhodium complexes [4,9]. Exceptions to this behaviour are observed for $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuH}_3(\text{PPh}_3)_3$ which are more susceptible to hydrolytic decomposition. When aqueous NaOH or acetic acid are used as additives, a similar increase in the reaction rate is observed but the selectivity for isopropanol is lowered considerably, as a result of the formation of high-boiling aldol condensation products, predominantly diacetone alcohol; this contrasts with the behaviour of rhodium systems which in the presence of strong base reduce acetone to isopropanol with selectivities of ca. 99% [13]. Strohmeier and Weigelt claimed a beneficial effect of acid and basic additives on the rate of hydrogenation of ketones with $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{Ru}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ without decreasing the selectivity for the desired alcohol from a value of 99% [23].

TABLE 1
HYDROGENATION OF ACETONE WITH RUTHENIUM COMPLEX CATALYSTS
([Substrate] : [Catalyst] = 1,300; 150°C ; 68 atm H_2 ; 4 h)

Complex	Conversion ^a (%)	Selectivity ^a (%)	Conversion ^b (%)	Selectivity ^b (%)
$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	95	95	25	93
$\text{RuH}(\text{NO})(\text{PPh}_3)_3$	97	95	22	96
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_3$	90	92	26	87
$\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3$	69	94	67	100
$\text{Ru}(\text{H})_2(\text{PPh}_3)_4$	39	82	56	98
$\text{RuCl}_2(\text{PPh}_3)_3$	33	83	18	82
$\text{Ru}(\text{H})_4(\text{PPh}_3)_3$	30	86	78	100
$\text{RuHCl}(\text{PPh}_3)_3$	13	70	6	70
$\text{Ru}_3(\text{CO})_{12}$	3	41	6	69

^a 2.5% H_2O added. ^b Dry.

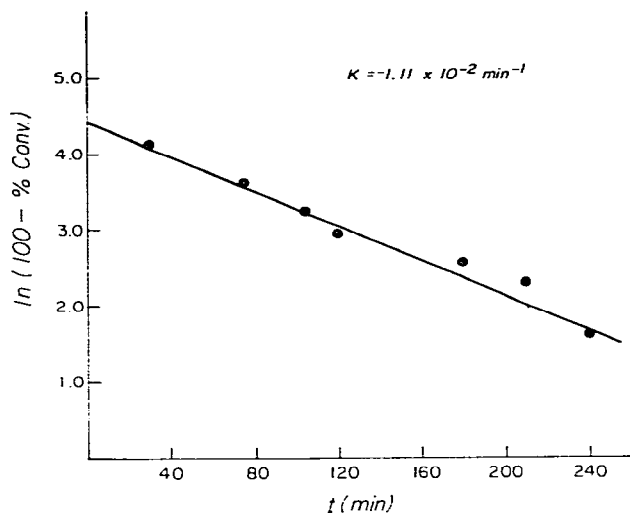


Fig. 1. Hydrogenation of acetone with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. Rate dependence on the substrate concentration. $([(\text{CH}_3)_2\text{CO}] : [\text{Ru}] = 1,300; 150^\circ\text{C}; 68 \text{ atm } \text{H}_2; 2.5\% \text{ H}_2\text{O})$.

Kinetics of the hydrogenation of acetone with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$

Acetone can be effectively reduced to isopropanol with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ at 150°C and 68 atm H_2 in the presence of small amounts of water. The reaction is first order with respect to the organic substrate concentration ($k = 1.11 \times 10^{-2} \text{ min}^{-1}$) as shown in Fig. 1. Starting with a substrate : catalyst ratio of 100,000, turnover numbers of ca. 15,000 have been achieved after 3 days reaction, showing that the initial activity (200–250 mol acetone reduced per mol of catalyst per hour) does not decrease appreciably with reaction time. The catalyst precursor is transformed during the reaction into mixtures which are difficult to separate, but these mixtures can be re-used and they show very similar catalytic properties to those of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$.

Effect of temperature. Results of hydrogenating acetone with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ at various temperatures within the range $80\text{--}150^\circ\text{C}$ are shown in Table 2. Below 80°C hydrogenation is very slow and at about 200°C the complex begins to decompose. The selectivity for isopropanol increases with increasing temperature, indicating that the hydrogenation reaction becomes much faster

TABLE 2

HYDROGENATION OF ACETONE WITH $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. THE INFLUENCE OF TEMPERATURE
 $([(\text{CH}_3)_2\text{CO}] : [\text{Ru}] = 1300; 68 \text{ atm. } \text{H}_2; 2.5\% \text{ H}_2\text{O}; 4 \text{ h})$

T ($^\circ\text{C}$)	Conversion (%)	Selectivity (%)
80	21	73
100	42	88
120	70	94
150	95	95

TABLE 3

HYDROGENATION OF ACETONE WITH $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. THE EFFECT OF PRESSURE($[(\text{CH}_3)_2\text{CO}] : [\text{Ru}] = 1300 : 150^\circ\text{C} : 2.5\% \text{H}_2\text{O} : 4 \text{ h}$)

P (atm)	Conversion (%)	Selectivity (%)
17	60	92
51	89	93
68	95	95
100	98	97

than aldol condensation. At 150°C the reaction rate is appropriate for a kinetic investigation.

Effect of pressure. Table 3 and Fig. 2 show the effect of hydrogen pressure on the hydrogenation of acetone with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$; both the rate of the reaction and the selectivity for isopropanol are enhanced by increasing hydrogen pressure in the range 17–100 atm. Below 10 atm the rate of the reaction is unappreciable.

The reaction was found to be first order with respect to hydrogen pressure ($k = 1.67 \times 10^{-1} \text{ min}^{-1}$) by measuring the pressure drop while keeping all the other parameters constant. This indicates that oxidative addition of dihydrogen to a low-valent ruthenium intermediate is an important step in the catalytic cycle.

Effect of catalyst concentration. The reaction was determined to be first order with respect to the concentration of the catalyst ($k = 4.40 \times 10^{-1} \text{ l mol}^{-1} \text{ min}^{-1}$) by carrying out a series of experiments (interrupted after an arbitrarily chosen period of 2 hours), in which the catalyst concentration was varied over a suitable range and all the other parameters were kept constant (Fig. 3).

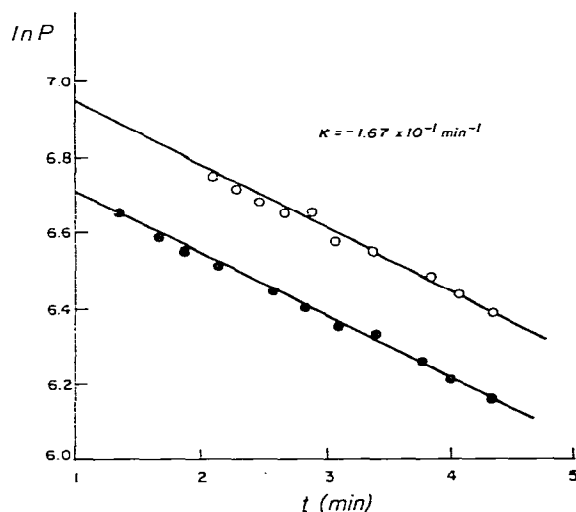


Fig. 2. Hydrogenation of acetone with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. Rate dependence on the hydrogen pressure. ($[(\text{CH}_3)_2\text{CO}] : [\text{Ru}] = 1,300 ; 150^\circ\text{C} ; \bullet = 68 \text{ atm}, \circ : 85 \text{ atm} ; 2.5\% \text{H}_2\text{O}$).

First order dependence on catalyst and substrate concentration as well as on hydrogen pressure has been reported for the hydrogenation of cyclohexane in presence of $H_4Ru_4(CO)_{12}$ [19]. No kinetic measurements have been reported for mononuclear ruthenium complexes.

Effect of water concentration. Fig. 4 shows the effect of water on the rate of hydrogenation of acetone with $RuHCl(CO)(PPh_3)_3$. The reaction is first order with respect to the concentration of water ($k = 4.8 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$) within the range investigated (0.5-5% by vol.); this indicates that water assists either the formation of the catalytically active species or its decomposition to the product alcohol. At higher concentrations of water (10% or greater) the rate of consumption of acetone is even faster, but the selectivity for isopropanol decreases considerably as a result of condensation reactions, and the measurements are no longer indicative of the hydrogenation process alone.

Schrock and Osborn found [4] that the beneficial effect of water on the rate of hydrogenation of acetone with cationic rhodium complexes reached a maximum at concentrations of ca. 1%, and further addition of water caused a slight decrease in the rate; a water-assisted hydrogen transfer to a coordinated alkoxy group was suggested as an explanation for this effect. Solodar reported [9] a similar observation when studying the asymmetric hydrogenation of ketones with cationic rhodium complexes with chiral ligands; the maximum rates were obtained at about 1% water concentration, and the maximum optical purity at a water level of 0.1%. By contrast, Ojima et al. observed [11] that small quantities of water did not affect the rate of the asymmetric hydrogenation of ketones with neutral rhodium complexes; furthermore, the extent of asymmetric induction was lowered by water.

It thus seems that the effect of water on our catalytic system is quite unique, since we do not observe a tendency towards a maximum in the rate with increasing amounts of water; the choice of a specific water concentration is then provided by selectivity considerations alone. As to the precise manner in

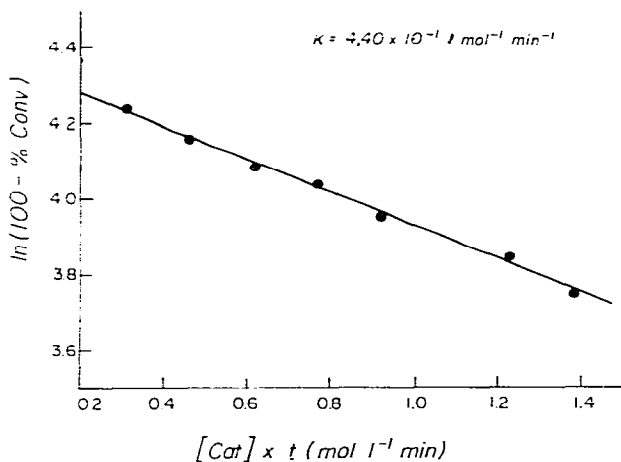


Fig. 3. Hydrogenation of acetone with $RuHCl(CO)(PPh_3)_3$. Rate dependence on the catalyst concentration. (150°C , 68 atm H_2 ; 2.5% H_2O ; 2 h).

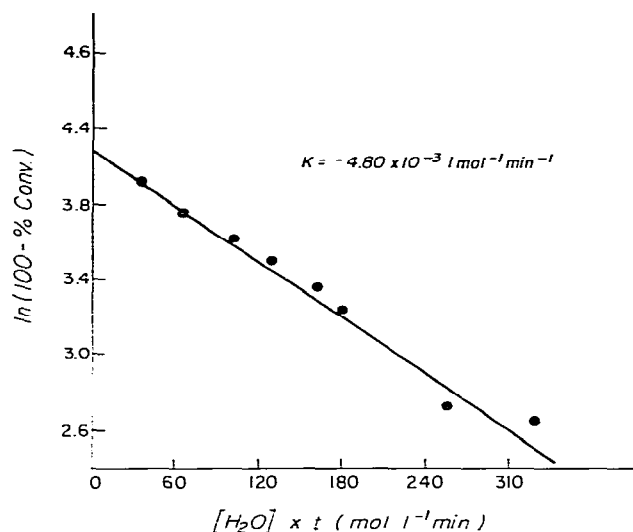


Fig. 4. Hydrogenation of acetone with $RuHCl(CO)(PPh_3)_3$. Rate dependence on the concentration of water. ($[CH_3)_2CO] : [Ru] = 1,300$; $150^\circ C$; 68 atm H_2 ; 2 h).

which water assists the reaction, we are at present unable to propose a mechanism.

Hydrogenation of other ketones with $RuHCl(CO)(PPh_3)_3$

The complex $RuHCl(CO)(PPh_3)_3$ catalyses the hydrogenation of other ketones to their corresponding alcohols under the same reaction conditions as for reduction of acetone (Table 4). The lower conversions observed are probably due to increasing steric congestion about the C=O bond.

Experimental

Materials

Acetone, 3-pentanone, acetophenone and cyclohexanone (Merck) were dried over molecular sieves and distilled under nitrogen immediately before use. Ruthenium trichloride hydrate, dodecacarbonyltriruthenium and triphenylphosphine (Strem Chemicals) were used as received. The complexes $RuHCl$ -

TABLE 4

HYDROGENATION OF KETONES WITH $RuHCl(CO)(PPh_3)_3$. EFFECT OF THE NATURE OF THE SUBSTRATE

($[Ketone] : [Ru] = 1300$; $150^\circ C$; 68 atm H_2 ; 2.5% H_2O ; 4 h)

Substrate	Conversion (%)	Product (Selectivity) (%)
Cyclohexanone	56	Cyclohexanol(96)
Acetophenone	39	1-Phenylethanol(94)
3-Pentanone	32	Pentan-3-ol(98)

(CO)(PPh₃) [24], RuH(NO)(PPh₃)₃ [25], RuCl₂(CO)₂(PPh₃)₂ [26], Ru(H)₂(CO)(PPh₃)₃ [24], Ru(H)₂(PPh₃)₄ [27], RuCl₂(PPh₃)₃ [28], Ru(H)₄(PPh₃)₃ [29] and RuHCl(PPh₃)₃ [30] were prepared by published methods.

Hydrogenation experiments

The catalyst (0.2 mmol), the ketone (275 mmol), water (2.5% by vol.) and a stirring bar were introduced into a glass-lined stainless steel autoclave (70 ml). Air was removed by flushing three times with dry nitrogen, and the autoclave was heated to the required temperature in a thermostatted silicone oil bath for ca. 1 h. Hydrogen was then continuously admitted from a high-pressure reservoir to maintain a constant desired pressure throughout the reaction. No appreciable differences were noted in the reaction if the catalyst was introduced in a sealed glass vial and brought into contact with the substrate after thermal equilibrium had been reached at the appropriate hydrogen pressure. Reactions were quenched by rapid cooling in ice, and the products immediately analyzed using a Varian 3720 gas chromatograph fitted with a 6 ft 10% Carbowax 20M on 80/100 chromosorb W AW column and a flame ionization detector. Peak areas were obtained with a Varian CDS-111 data system. Reactions were carried out at least three times to avoid spurious results.

Curves obtained from the kinetic measurements were fitted by a least squares method, all yielding r^2 values greater than 0.98.

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