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HOMOGENEOUS HYDROGENATION OF ALDEHYDES TO ALCOHOLS WITH RUTHENIUM COMPLEX CATALYSTS *

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Summary

A number of ruthenium complexes catalyse the reduction of aldehydes to their corresponding alcohols in toluene solution under mild reaction conditions. The most convenient catalyst precursor is hydridochlorocarbonyltris-(triphenylphosphine)ruthenium(II). Turnover numbers up to 32 000 have been achieved with this catalyst. The rate of hydrogenation is first order with respect to the substrate concentration, the catalyst concentration and the hydrogen pressure, and is also affected by acid and basic additives.

Introduction

The homogeneous reduction of aldehydes to alcohols catalysed by cobalt [2], rhodium [3—5] and iridium [6,7] compounds has been described in some detail. Ruthenium complexes, on the other hand, have seldom been used in this reaction.

Imai et al. reported the transfer hydrogenation of aldehydes using $Ru(H)_2(PPh_3)_4$ [8]; Wilkinson and co-workers mentioned the reduction of propionaldehyde with the hydroformylation catalyst $Ru(CO)_3(PPh_3)_2$ [9], whilst Tsuji and Suzuki reduced several aldehydes using $RuCl_2(PPh_3)_3$ [10]. While this work was in progress Strohmeier and Wiegelt reported the use of $RuCl_2(CO)_2(PPh_3)_2$ for the hydrogenation of aliphatic and aromatic aldehydes [11].

In a recent paper we described the reduction of ketones with ruthenium catalysts [12]. We now wish to report the results of our studies on the catalytic activity of a series of ruthenium complexes for the homogeneous hydrogenation of aldehydes to their corresponding alcohols, which can be effected under

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* Preliminary communication, ref. 1.

much milder reaction conditions. A detailed study of the influence of the various reaction parameters on the properties of the best catalyst precursor, viz. hydridochlorocarbonyltris(triphenylphosphine)ruthenium(II), $RuHCl(CO)(PPh_3)_3$, has been carried out. Kinetic measurements under appropriate reaction conditions are reported.

Results

The catalysts

Table 1 shows the results of the hydrogenation of propionaldehyde with a series of ruthenium complexes in toluene solution under 30 atm H_2 at 80° C. $RuHCl(CO)(PPh_3)_3$ was found to be the most convenient catalyst precursor, since apart from showing high activity and selectivity its preparation is very simple [15] and its stability towards oxygen very high. $RuHCl(PPh_3)_3$, although a more active catalyst, requires inert atmosphere manipulation in solution; furthermore, this complex (and indeed all other compounds tested not containing carbonyl ligands) promotes competing decarbonylation of the aldehyde, as evidenced by the isolation of metal carbonyl species at the end of the reaction. The compounds previously reported to hydrogenate aldehydes, viz. $RuH_2(PPh_3)_4$ [8], $RuCl_2(PPh_3)_3$ [10] and $RuCl_2(CO)_2(PPh_3)_2$ [11] proved to be less active and selective than our chosen precursor $RuHCl(CO)(PPh_3)_3$ under our reaction conditions, the lack of selectivity being mainly due to the appearance of aldol condensation products.

Hydrogenation of aldehydes with $RuHCl(CO)(PPh_3)_3$

The hydrogenation of propionaldehyde can be carried out smoothly with $RuHCl(CO)(PPh_3)_3$ in toluene solution under 30 atm H_2 at 80° C to yield 1-propanol as the only product detectable by GLC analysis of the gaseous and liquid fractions. No appreciable amounts of involatile or high boiling residues were found on evaporating the reaction mixtures. At higher temperatures complete conversion is achieved in ca. 1 h (Fig. 1); starting with a substrate to

TABLE 1

HYDROGENATION OF PROPIONALDEHYDE WITH RUTHENIUM COMPLEX CATALYSTS

([Aldehyde] = 2 *M*; [catalyst] = 2 m*M*; 80° C; 30 atm H_2; 90 min)

Complex	Conversion (%)	Selectivity [a] (%)
$RuHCl(CO)(PPh_3)_3$	50(65) [b]	100
$RuHCl(PPh_3)_3$	98	100
$RuCl_2(PPh_3)_3$	67	50
$Ru(H)_4(PPh_3)_3$	13	72
$RuCl_2(CO)_2(PPh_3)_2$	10	68
$Ru(H)_2(CO)(PPh_3)_3$	10	61
$Ru(H)_2(PPh_3)_4$	9	67
$RuH(NO)(PPh_3)_3$	7	100
$Ru_3(CO)_{12}$	1	100

[a] Throughout this paper selectivity calculated as % of total product yield. [b] [aldehyde] : [catalyst] = 50 000; 140° C; 50 h.

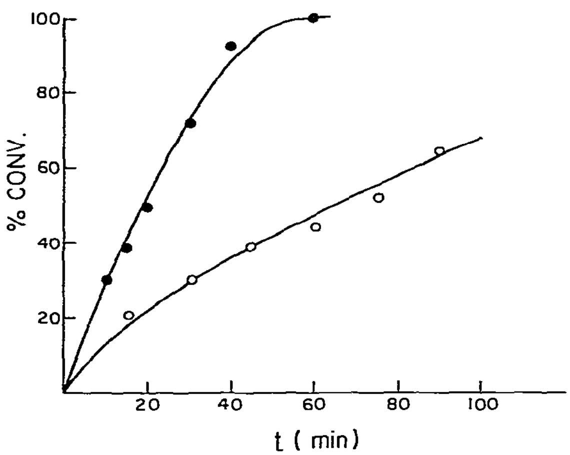


Fig. 1. Hydrogenation of propionaldehyde with $RuHCl(CO)(PPh_3)_3$ ([aldehyde] = 2 *M*; [catalyst] = 2 m*M* in toluene; 30 atm H_2; ○: 80°C; ●: 140°C).

catalyst ratio of 50 000 we have achieved turnover numbers of up to 32 000 after 50 h continuous reaction at 140°C (Table 1). The catalyst is transformed during the reaction into a mixture of ruthenium species which we have not been able to separate in a pure form; these mixtures, however, have been re-used and they show virtually the same activity as the parent compound for the hydrogenation reaction.

The influence of temperature is further noted in Table 2; at 25°C the reaction is very slow and about 200°C the complex begins to decompose. The rate of the reaction at 80°C is appropriate for kinetic measurements.

Kinetics of the hydrogenation reaction

The reaction order with respect to the concentration of the organic substrate was determined from a series of reactions carried out under constant hydrogen pressure and interrupted at various degrees of conversion by rapid cooling in ice. First order dependence on aldehyde concentration ($k = -9.4 \times 10^{-3}$ min^{-1}) was observed, as shown in Fig. 2.

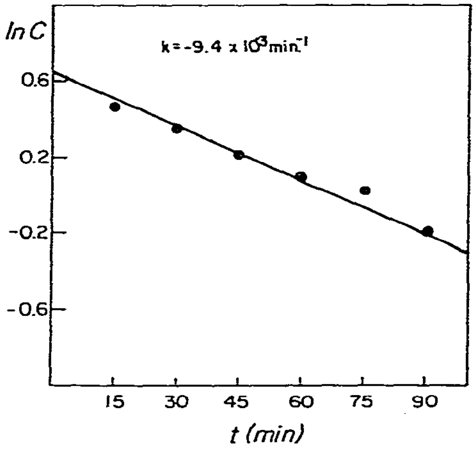
The hydrogenation reaction was also found to be first order with respect to

TABLE 2

HYDROGENATION OF PROPIONALDEHYDE WITH $RuHCl(CO)(PPh_3)_3$: THE INFLUENCE OF TEMPERATURE

([aldehyde] = 2 *M*; [catalyst] = 2 m*M* in toluene; 30 atm H_2; 30 min)

T (°C)	Conversion (%)
60	17
80	33
100	45
120	65
140	84



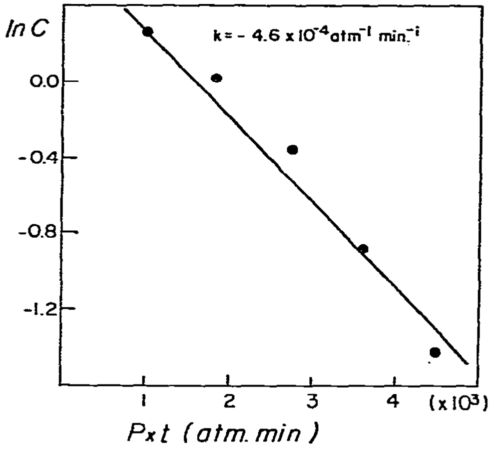


Fig. 2. Hydrogenation of propionaldehyde with $RuHCl(CO)(PPh_3)_3$: Rate dependence on substrate concentration (C = [aldehyde]; $C_0 = 2\ M$, [catalyst] = 2 mM in toluene; 30 atm H_2; 80°C).

Fig. 3. Hydrogenation of propionaldehyde with $RuHCl(CO)(PPh_3)_3$: Rate dependence on hydrogen pressure (C = [aldehyde]; $C_0 = 2\ M$, [aldehyde] = 2 mM in toluene; 80°C. 90 min).

TABLE 3

HYDROGENATION OF PROPIONALDEHYDE WITH $RuHCl(CO)(PPh_3)_3$: THE EFFECT OF PRESSURE

([aldehyde] = 2 M; [catalyst] = 2 mM in toluene; 80°C; 90 min)

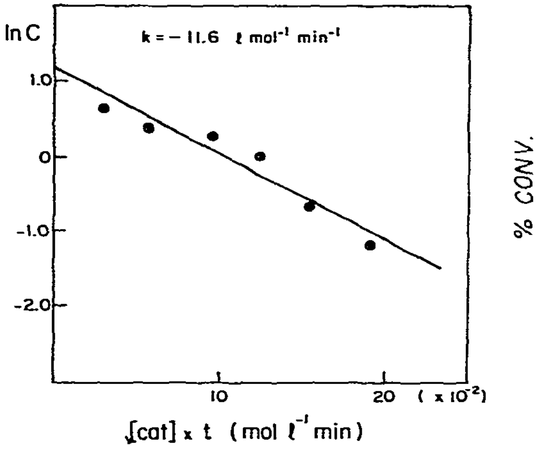
P (atm)	Conversion (%)
10	35
20	54
30	65
40	83
50	88

TABLE 4

HYDROGENATION OF PROPIONALDEHYDE WITH $RuHCl(CO)(PPh_3)_3$: EFFECT OF ADDITIVES

([Aldehyde] = 2 M; [Catalyst] = 2 mM; [additive] = 1% by vol.; 80°C; 30 atm H_2; 60 min)

Additive	Conversion (%)	Selectivity (%)
None	50	100
NaOH	74	12
H_2O	73	100
CH_3COOH	62	96
$(C_2H_5)_3N$	28	47



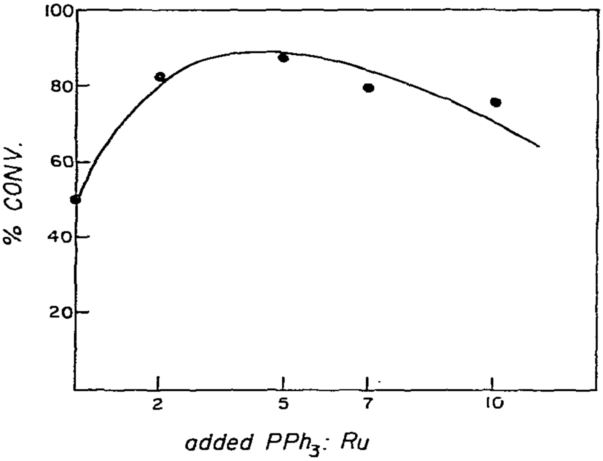


Fig. 4. Hydrogenation of propionaldehyde with $RuHCl(CO)(PPh_3)_3$; Rate dependence on catalyst concentration (C = [aldehyde]; C_0 = 2 M in toluene; 30 atm H_2; 80°C; 60 min).

Fig. 5. Hydrogenation of propionaldehyde with $RuHCl(CO)(PPh_3)$: Effect of excess triphenylphosphine ([aldehyde] = 2 M; [catalyst] = 2 mM in toluene; 30 atm H_2; 80°C; 60 min).

the hydrogen pressure (k = —4.6 × 10^{-4} atm^{-1} min^{-1}) (Table 3 and Fig. 3) and catalyst concentration (k = —11.6 l mol^{-1} min^{-1}) (Fig. 4) by carrying out two series of experiments (interrupted after an arbitrarily chosen period of time) in which the reaction parameter under investigation was varied over a suitable range, while all the others were kept constant.

The influence of additives

Results collected in Table 4 show the influence of small amounts of various additives. Triethylamine has a detrimental effect on both the activity and selectivity of the reaction; sodium hydroxide enhances the rate of hydrogenation but also promotes aldol condensation, resulting in poor selectivity for 1-propanol. Water and acetic acid accelerate the reaction without markedly increasing the amounts of by-products.

The effect of excess triphenylphosphine

The effect of the presence of excess phosphine on the rate of aldehyde hydrogenation is shown in Fig. 5. An unexpected increase in the conversion to 1-propanol is observed up to a ratio of phosphine to ruthenium of about 5 to 1; at higher phosphine concentrations the extent of hydrogenation decreases. The selectivity does not vary significantly with phosphine concentration.

Discussion

Although a number of ruthenium complexes can promote the reduction of aldehydes to alcohols, the most convenient precursor is $RuHCl(CO)(PPh_3)_3$ which hydrogenates aldehydes with high turnover numbers and selectivities under rather mild reaction conditions. This catalyst may thus be considered superior to all the other ruthenium complexes previously reported to hydrogenate aldehydes [8—11].

The rate of hydrogenation of propionaldehyde under the conditions used is directly proportional to the concentration of the substrate and the catalyst, and to the hydrogen pressure. This is, to our knowledge, the first report of a kinetic investigation of this reaction, but a similar dependence has been found in the related hydrogenation of ketones with mononuclear [12] and polynuclear [13] ruthenium compounds.

The rate of the reaction is also affected by acid and basic additives. The poisoning effect of triethylamine is probably due to strong coordination which blocks the sites required for the aldehyde to react. The beneficial effect of water and acetic acid has been observed in the hydrogenation of ketones with ruthenium [12] and rhodium catalysts [14], and in the reduction of aldehydes with iridium systems [6,7]; this has been explained either by formation of catalytically active hydrido-acetate complexes or by a mechanism involving a hydrolytic decomposition of a metal alkoxide intermediate. The latter seems a more plausible explanation in our case, as we have infrared evidence that no acetate species are formed under these conditions. More interestingly, addition of small amounts of excess triphenylphosphine resulted in increased conversions, which was unexpected as a phosphine dissociation step is usually assumed to be part of the catalytic hydrogenation cycle; indeed, a marked decrease in catalytic activity for olefin hydroformylation was observed with incremental addition of triphenylphosphine to ruthenium complexes [9]. Since we have so far been unable to separate the various ruthenium species which are produced during the hydrogenation reaction we cannot offer a detailed explanation for this effect. It is possible, however, that some of these compounds are catalytically inactive and therefore the observed activity corresponds to only a fraction of the ruthenium initially used; addition of triphenylphosphine may then displace the equilibrium in such a way as to inhibit the formation of the inactive species, resulting in higher conversions. When the concentration of free phosphine becomes too high, coordinatively saturated species are probably present in a larger proportion and the rate of the hydrogenation reaction again is decreased. A similar effect has been observed in the hydrogenation of aldehydes with cobalt carbonyl complexes [2].

Experimental

Materials

Propionaldehyde (Merck) was purified by distillation under nitrogen. Ruthenium trichloride hydrate, dodecacarbonyltriruthenium and triphenylphosphine (Strem Chemicals) were used as received. The complexes $RuHCl(CO)(PPh_3)_3$ [15], $RuH(NO)(PPh_3)_3$ [16], $RuCl_2(CO)_2(PPh_3)_2$ [17], $Ru(H)_2(CO)(PPh_3)_3$ [15], $Ru(H)_2(PPh_3)_4$ [18], $RuCl_2(PPh_3)_3$ [17], $Ru(H)_4(PPh_3)_3$ [19] and $RuHCl(PPh_3)_3$ [20] were prepared by published methods.

Hydrogenation reactions

The catalyst (0.1 mmol), the aldehyde (0.1 mol), toluene (to a total volume of 50 ml) and a stirring bar were introduced into a glass-lined stainless steel autoclave (Parr Instruments, 120 ml). The autoclave was flushed three times with hydrogen, charged to the desired pressure and then heated in a thermostatted silicone oil bath. Stirring was started immediately and this was taken as the zero time for the reaction. Hydrogen was continuously admitted from a high pressure reservoir to maintain a constant pressure during each experiment. Reactions were quenched by rapid cooling in ice and the products immediately analyzed using a Varian 3720 gas chromatograph fitted with a flame ionisation detector and an SE-30 column.

No appreciable differences were noted in the measurements if the catalyst was introduced in a sealed glass vial and brought into contact with the aldehyde after thermal equilibrium had been reached at the appropriate pressure (we estimate a time of 1—2 min for this equilibrium to be reached).

Reactions were carried out at least three times in different reactors to ensure reproducibility of the results. Plots of kinetic measurements were fitted by a least squares method yielding r^2 values greater than 0.95 in all cases.

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