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CATALYSIS BY PHOSPHINE COBALT CARBONYL COMPLEXES

V. KINETICS OF HOMOGENEOUS CYCLOHEXENE HYDROGENATION CATALYZED BY $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$*

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SUMMARY

An investigation is described of the kinetics of homogeneous cyclohexene hydrogenation catalyzed by $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ under 30 atm of hydrogen and at 60°. The following rate equation fits the experimental data:

$$\text{Rate} = \frac{k'K_2[H_2][\text{Cat}][S]}{1+K_2[S]+[PR_3]/K_1}$$

where $[S]$, $[H_2]$, $[\text{Cat}]$ and $[PR_3]$ are the concentrations of olefin, hydrogen, catalyst, and free phosphine, respectively; k' is the rate constant of the rate determining step and K_1 and K_2 are appropriate equilibrium constants. The mechanism of the reaction is discussed in the light of this and previously reported information.

INTRODUCTION

We recently described the synthesis and catalytic properties of some Co^I hydrido[1] and Co^0 cluster[2] carbonyl tributylphosphine complexes. The hydrides of formula $CoH(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n$ ($n=2, 3$) are hydrogenation catalysts for aldehydes, olefins and alkynes under moderate conditions ($p_{H_2}=20$–30 atm; 40–115°)[1]. They also catalyze isomerization, the rate of which is often comparable with that of hydrogenation.

The hydrogenating properties of these complexes are important; they may possibly be formed in small amounts during the phosphine-modified cobalt carbonyl hydroformylation process, which gives rise mainly to alcohols. In recent years a large number of investigations have been devoted to the elucidation of the mechanisms of homogeneous hydrogenation (this subject has been recently reviewed[3,4]). We carried

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* Parts I and III were published in this Journal (see refs. 1 and 2); for parts II and IV see refs. 11 and 12.

out the present kinetic study with the aim of throwing further light on the previously suggested mechanism[1] of hydrogenation, and of extending the knowledge of homogeneous hydrogenation processes in general.

Cyclohexene was chosen as substrate in order to avoid any possible side reactions, such as double bond isomerization or stoichiometric hydroformylation*. It is particularly important to avoid the latter, since when stoichiometric hydroformylation takes place (*e.g.* with α-olefins) a green compound is formed *in situ* from $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$. This green compound, which has not been fully identified, but which is probably a cluster[2], has a very high activity as a hydrogenation catalyst.

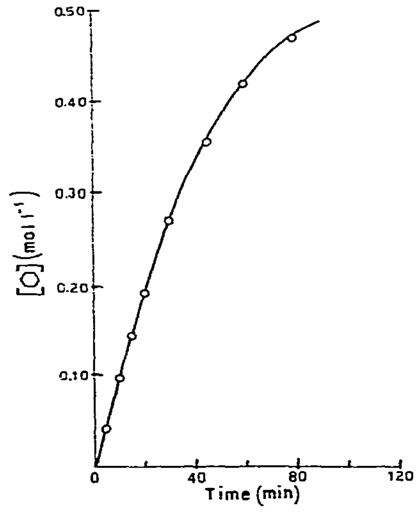
RESULTS

The kinetic investigation was carried out in hexane at temperatures between 100° and 150° and pressures between 10 and 40 atm.

A large range of concentrations of cyclohexene, cobalt catalyst and free phosphine was examined, but the initial rates were used to determine the rate law, as in other similar studies[5,6]. This procedure avoids any possible influence due to slow side reactions of the substrate or of the catalyst, although these were, in any case, minimized in our studies by use of cyclohexene as substrate.

Hydrogen-uptake experiments

The hydrogen-uptake was followed by measuring either the pressure drop or the cyclohexane formation. In Fig. 1 the amount of cyclohexane formed (which corresponds to the hydrogen absorbed) is plotted against the time. It will be seen that



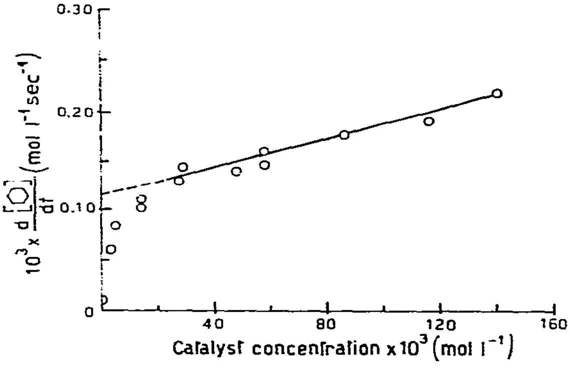


Fig. 1. A typical hydrogenation of cyclohexene using $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$. Solvent hexane; olefin concn. 1 mol l^{-1}; catalyst concn. 5.7×10^{-2} mol l^{-1}; temp. 130°; hydrogen pressure 30 atm.

Fig. 2. Rate of hydrogenation of cyclohexene as a function of catalyst concentration. Solvent hexane; olefin concn. 1 mol l^{-1}; temp. 130°; hydrogen pressure 30 atm.

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* Cyclohexene, being an internal olefin, does not readily undergo hydroformylation.

the initial rate is fairly constant in the presence of excess cyclohexene. In all cases the experiments were mainly reproducible to within ±5%, and the rates were obtained from the tangents to plots of the type shown in Fig. 1.

In all the experiments clear solutions were obtained after completion of the reaction, showing that there is no formation of a heterogeneous catalyst such as finely dispersed metallic cobalt.

Dependence on catalyst concentration

The experimental data are shown in Fig. 2. The linear trend obtained with catalyst concentrations higher than 2×10^{-2} mol l^{-1} suggests a pseudo first order dependence.

The occurrence of relatively higher rates at lower concentrations was reported by Wilkinson and coworkers in their studies of olefin hydrogenation using $RhH(CO)(PPh_3)_3$ and $RhCl(PPh_3)_3$[5,6]; in both cases they invoked a two-step dissociative process of the phosphine ligands bound to the catalyst to form co-ordinatively unsaturated species, with the second step taking place only in dilute solutions. Interestingly, analogous behaviour was also observed in the homogeneous hydrogenation of maleic acid by means of $IrX(CO)(PPh_3)_2$ (X = Cl, Br)[7].

Dependence on hydrogen pressure

Hydrogenations under standard conditions and at various hydrogen pressures result in a linear plot of the rate against pressure with zero intercept (Fig. 3). Hence, assuming Henry's Law, a linear dependence of the reaction rate on the hydrogen concentration in solution is demonstrated.

Dependence on cyclohexene concentration

In a typical cyclohexene hydrogenation under standard conditions with a large excess of olefin the reaction is almost zero order(or pseudo zero order) in olefin concentration up to 25–30% conversion, but then starts to show an order higher than zero (Fig. 1). These preliminary observations suggest that the relation between rate and olefin concentration must be complex, unless our results are subject to some

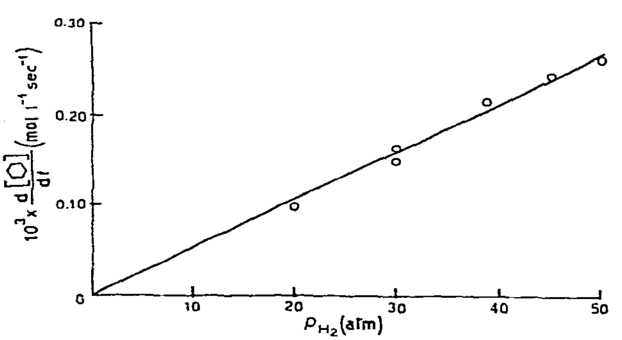


Fig. 3. Rate of hydrogenation of cyclohexene as a function of hydrogen pressure. Solvent hexane; olefin concn. 1 mol l^{-1}; catalyst concn. 5.7×10^{-2} mol l^{-1}; temp. 130°.

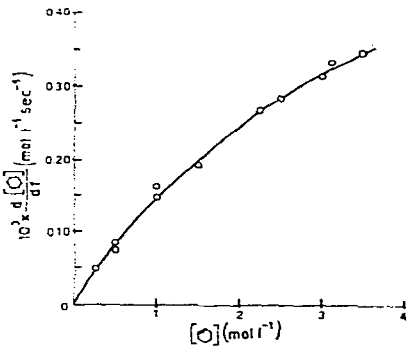
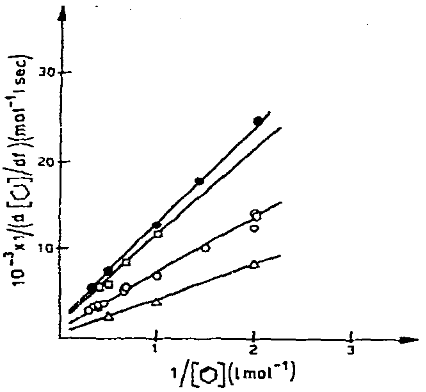


Fig. 4. Rate of hydrogenation as a function of olefin concentration. Solvent hexane; catalyst concn. 5.7×10^{-2} mol l^{-1}; temp. 130°; hydrogen pressure 30 atm.



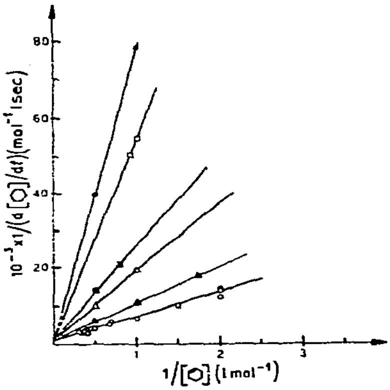


Fig. 5. Plot of reciprocal of the rate of hydrogenation of cyclohexene against the reciprocal of the olefin concentration. Solvent hexane; catalyst concn. 5.7×10^{-2} mol l^{-1}; hydrogen pressure 30 atm; temp. (●) 120±0.5°; (□) 122±0.5°; (○) 130±0.5°; (△) 138±0.5°.

Fig. 6. Plot of reciprocal of the rate of hydrogenation of cyclohexene against the reciprocal of the olefin concentration at different free phosphine concentrations. Solvent hexane; catalyst concn. 5.7×10^{-2} mol l^{-1}; temp. 130°; hydrogen pressure 30 atm; free phosphine concentration ($10^3 \times$ mol l^{-1}) (●) 57; (□) 40; (■) 20; (△) 15; (▲) 7; (○) 0.

TABLE 1

Constants C and C^* derived from the plot of Fig. 5, and the calculated values of k'. Solvent: hexane; catalyst concn.: 5.7×10^{-2} mol l^{-1}; hydrogen pressure: 30 atm.

Temperature (°C)	$10^{-3} \times C$ (*sec*)	$10^{-3} \times C^*$ (*mol*$^{-1}$ *l sec*)	$10^2 \times k'$ (*mol*$^{-1}$ *l sec*$^{-1}$)
120±0.5	11.0	2.08	3.19
122±0.5	9.9	1.81	3.62
130±0.5	6.2	1.07	5.83
138±0.5	3.7	0.62	9.56

TABLE 2

Data derived from Fig. 6.
Solvent: hexane; catalyst concn.: 5.7×10^{-2} mol l^{-1}; temp.: 130°; hydrogen pressure: 30 atm.

Added phosphine concentration ($10^3 \times$ *mol* l^{-1})	$10^{-3} \times C$ (*sec*)	$10^{-3} \times C^*$ (*mol*$^{-1}$ *l sec*)	C/C^* (*mol* l^{-1})
0	6.2	1.07	5.8
7	9.2	1.07	8.6
15	18.1	1.07	16.9
20	24.6	1.07	23.2
40	54.0	1.07	50.1
57	77.0	1.07	72.0

unrecognised side-reaction of the catalyst during the conversion of the olefin.

We thus investigated the rate dependence on substrate concentration and observed, in agreement with other authors[5], that the rate approaches an asymptotic value with increasing olefin concentration (Fig. 4). The plot of the reciprocal of the rate against the reciprocal of olefin concentration is linear (Fig. 5), with a positive intercept on the y-axis. These results are consistent with the following equation:

$$\frac{1}{R} = C\frac{1}{[\text{cyclohexene}]} + C^*$$

where R is the reaction rate and C and C^* are the parameters of the linear plots shown in Fig. 5. Values of C and C^* obtained at different temperatures are listed in Table 1.

Dependence on free phosphine concentration

An excess of free tributylphosphine reduces the hydrogenation rate; in Fig. 6 the reciprocal of the hydrogenation rate is plotted against the reciprocal of the olefin concentration at different concentrations of added free phosphine. It will be seen that a relatively small addition of free phosphine has a large effect; for instance with 5.7×10^{-2} mol l^{-1} catalyst concentration, a concentration of free phosphine of 1.5×10^{-2} mol l^{-1} results in a threefold decrease of the olefin hydrogenation rate. The effect is evident when we consider the data listed in Table 2. As already reported by many authors[5,6,7], this effect must be ascribed to the suppression of the dissociation of phosphine from the catalytic complex to form vacant coordination sites.

Dependence on the temperature

The effects of temperature variation have been shown in Fig. 5 and Table 1. In Table 1 are also given the calculated rate constants for the rate determining step (see below). These constants give a linear Arrhenius plot, as shown in Fig. 7. The satisfactory linearity of the Arrhenius plot is in agreement with the assumption that under the reaction conditions only one catalytic species is involved.

The activation parameters are; $\Delta E_a = 20 \pm 1.5$ kcal mol^{-1}, $\Delta H = 19.2 \pm 1.5$ kcal mol^{-1} and $\Delta S = -17.2 \pm 3.9$ e.u. A comparison with the data reported for hydrogenation of cyclohexene in benzene ($\Delta H = 18.6$ kcal mol^{-1}, $\Delta S = 1.3$ e.u.) and of 1-hexene in benzene ($\Delta H = 18.6$ kcal mol^{-1}, $\Delta S = 1.1$ e.u.) using $\text{RhCl(PPh}_3)_3$[8] or for the hydrogenation of 1-hexene in benzene using $\text{RhH(CO)}_2(\text{PPh}_3)_2$[5] ($\Delta H = 10.6$ kcal

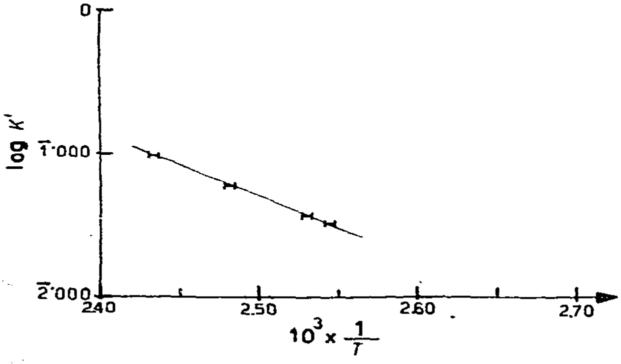


Fig. 7. Arrhenius plot of log k' against $10^3 \times 1/T$. (Data from Table 1.)

mol^{-1}, $\Delta S^{\neq} = -7.9$ e.u.), shows that the cobalt catalyst is associated with a less favourable energy and entropy of activation, which could account for the more drastic conditions required to carry out the hydrogenation; however, a solvent effect might also be involved[8].

Kinetic isotope effect

The rate of deuteration is comparable with or slightly greater than that of hydrogenation, the ratio k'_H/k'_D being 1/0.95, showing that the isotope effect is absent or slightly negative. In other hydrogenation reactions involving $RhCl(PPh_3)_3$ or $RhH(CO)_2(PPh_3)_2$, k_H/k_D ratios of 0.9–1.47 have been reported[5,6,8].

DISCUSSION

In a previous paper[1] we reported that in the presence of $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$, both hydrogenation and isomerisation of olefins proceed more quickly than hydrogen–deuterium scrambling between the preformed Co–D bond and the olefin; moreover the catalyzed H_2–D_2 exchange to form HD has a much lower rate than that of olefin hydrogenation. We thus suggested that olefin insertion into the Co–H bond is not an important step of the overall catalytic process of the hydrogenation or isomerization reactions.

The kinetic data reported in this paper can be interpreted[5,6] in terms of the following two schemes, where A is the cobalt complex:

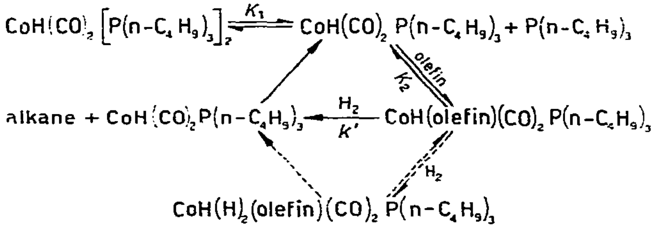
$$\mathrm{A} \overset{K_1}{\rightleftarrows} \mathrm{A}^* + \mathrm{L} \qquad \text{(dissociation of a phosphine to form a vacant site)}$$

$$(a) \qquad \mathrm{A}^* + \text{olefin} \overset{K_2}{\rightleftarrows} \mathrm{A}^*\text{olefin} \xrightarrow[\mathrm{H_2}]{\text{slow}} \mathrm{A}^* + \text{products}$$

$$(b) \qquad \mathrm{A}^* + \mathrm{H_2} \rightleftarrows \mathrm{A}^*\mathrm{H_2} \xrightarrow[\text{olefin}]{\text{slow}} \mathrm{A}^* + \text{products}$$

However, the slowness of the H_2–D_2 exchange shows that the reaction $A^* + H_2$ is too slow to be seriously considered. We can thus assume that mechanism (*a*) is operative. It corresponds to the following detailed Scheme 1. The rate equation can then be obtained. The concentration of the intermediate cobalt–olefin complex is related to the total concentration of the cobalt complexes through K_1 and K_2; thus we have:

SCHEME 1



$$[\mathrm{A}]_{\mathrm{tot.}} = [\mathrm{A}] + [\mathrm{A}^*] + [\mathrm{A}^*(\mathrm{S})] \qquad \text{(where S is the olefin)} \qquad (1)$$

$$K_2 = \frac{[A^*(S)]}{[A^*][S]} \tag{2}$$

and

$$K_1 = \frac{[A^*][L]}{[A]} \quad \text{(where L is the phosphine)} \tag{3}$$

Since the rate can be represented by the following equation:

$$R = -\frac{d[S]}{dt} = \frac{d[SH_2]}{dt} = k'[A^*(S)][H_2] \tag{4}$$

the rate equation may be rewritten as follows:

$$\text{Rate} = \frac{k'K_2[A]_{\text{tot.}}[H_2][S]}{1+K_2[S]+[L]/K_1} \tag{5}$$

The kinetic data are in agreement with this equation. The reaction order is in fact between one and zero* in the olefin, and linear plots (see Fig. 5) can be obtained by re-writing eqn. (5) in the following way:

$$\frac{1}{R} = \frac{1+[L]/K_1}{k'K_2[A]_{\text{tot.}}[H_2]} \cdot \frac{1}{[S]} + \frac{1}{k'[A]_{\text{tot.}}[H_2]} \tag{6}$$

The parameters C and C^* of the plot of Fig. 5 and eqn. (6) are given by eqns. (7) and (8):

$$C = \frac{1+[L]/K_1}{k'K_2[A]_{\text{tot.}}[H_2]} \tag{7}$$

and

$$C^* = \frac{1}{k'[A]_{\text{tot.}}[H_2]} \tag{8}$$

Thus from the C^* values we can evaluate k', the rate constant of the rate determining step (Table 1). Interestingly, the dependence of the rate on the total catalyst concentration is not linear at low concentrations (Fig. 2). This trend can be interpreted in terms of eqn. (5). In fact, since [L] is related to the concentration of the cobalt complexes by:

$$[L] = [A^*] + [A^*(S)] \tag{9}$$

it follows, on the basis of eqns. (2) and (3), that

$$[A] = \frac{[A^*][L]}{K_1} = \frac{[L]^2}{K_1(1+K_2[S])} \tag{10}$$

and

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* The order is around zero when

$$K_2[S] \gg 1 + \frac{1}{K_1}[L]$$

and around one when

$$1 + \frac{1}{K_1}[L] \gg K_2[S].$$

$$[A]_{tot.} = [A]+[L] = \frac{[L]^2}{K_1(1+K_2[S])} + [L]$$

$$= \frac{K_1}{1+K_2[S]} \cdot \frac{[L]^2}{K_1} + K_1 \frac{[L]}{K_1} \tag{11}$$

This implies a parabolic relation between $[A]_{tot.}$ and $[L]/K_1$; consequently when $[A]_{tot.}$ is small, a small variation of its value corresponds to a large change of the value of $[L]/K_1$. On the other hand, a similar variation leads to a very small and unimportant change in the case of higher concentrations of $[A]_{tot.}$.

It follows from the above discussion that at low total concentrations of the cobalt complex the term $[L]/K_1$ has an important effect on the rate, while the opposite is true at high catalyst concentrations; in this way the trends of Fig. 2 can be explained without invoking a subsequent dissociation of the active coordinatively unsaturated species[6]. Obviously a necessary condition is $[L]/K_1 \gg 1+K_2[S]$, that is $K_2 \gg K_1$.

This can be indirectly checked by use of the ratio (12), derived from equations (7) and (8):

$$\frac{C}{C^*} = \frac{1}{K_2} + \frac{[L]}{K_1 K_2} \tag{12}$$

This indicates the existence of a linear dependence of the ratio C/C^* on [L], from which K_1 and K_2 can be calculated.

In Fig. 8 is shown a plot of the ratio C/C^* against [L], the data of Table 2 being used. This plot is linear when the added phosphine concentration exceeds 1.5×10^{-2} mol l^{-1}; the deviation from linearity at low added phosphine concentrations can be ascribed to the free phosphine derived from the dissociation of the cobalt complex, which is negligible only when the concentration of the added phosphine is high.

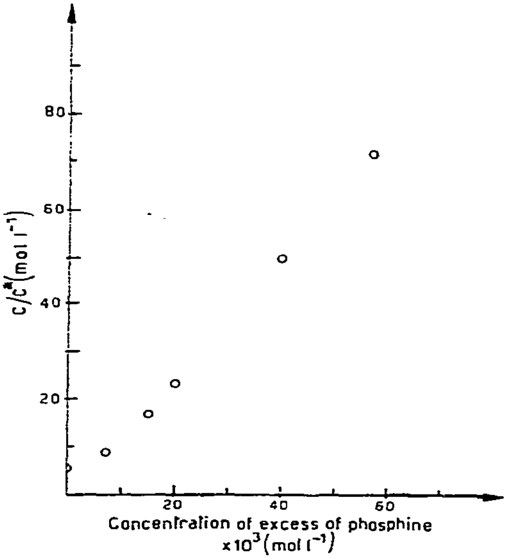

Fig. 8. Plot of C/C^* against the added phosphine concentration. (Data from Table 2.)

From Fig. 8 we can obtain $K_1K_2 = 0.8 \times 10^{-3}$ with acceptable accuracy; furthermore, from the experimental data in the absence of added phosphine, a value of 0.17 can be calculated for K_2. Since even in this case [L] is different from zero, it appears that $K_2 \geqslant 0.17$. Thus $K_1 \leqslant 1.58 \times 10^{-3}$, which agrees fairly well with the relation $K_2 \gg K_1$ and with the suggested slight dissociation of the cobalt complex.

CONCLUSION

In this paper we have established a fairly general scheme for the mechanism of cyclohexene hydrogenation catalyzed by $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$. There remains, however, an interesting point which cannot be settled simply from kinetic investigations, namely the mechanism of hydrogen interaction with the coordinated olefin, which is still a controversial subject. In their studies of hydrogenations catalyzed by $RhH(CO)_2(PPh_3)_2$[6] and $Ir(CO)(PPh_3)_2Cl$[7], Wilkinson and James, respectively, proposed an insertion into a metal–hydrogen bond to form the so-called half-hydrogenated σ-allyl, with this followed by the rupture of the metal–carbon σ-bond by molecular hydrogen either directly or after hydrogen activation by the metal.

In our case, there is a large amount of experimental evidence[1] that olefin insertion into the initial cobalt–hydrogen bond is not an important step; probably the intermediate involved is a hydrido–olefin complex in which the olefin is *trans* to hydrogen. A platinum–ethylene complex with this geometry has been in fact isolated, and it seems to be very stable[9]. We assume that the rate determining step is the direct hydrogen interaction with the cobalt-coordinated olefin in such an intermediate. The absence of a detectable isotope effect suggests that this interaction proceeds via instantaneous H_2 bond breaking and C–H bond making. However the kinetic and experimental evidence does not allow us to decide between the direct interaction of hydrogen with the olefin or previous hydrogen activation by the cobalt atom.

Recently kinetic studies[10] appeared on the olefin hydrogenation using $IrH(CO)(PPh_3)_3$. With this complex a slow hydrogen interaction to form $IrH_3(CO)(PPh_3)_2$ was reported, but this does not seem to be important in the overall mechanism of hydrogenation. In this case, as in ours, a direct hydrogen interaction with the coordinated olefin seems more probable.

EXPERIMENTAL

Materials and kinetic experiments

$CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ was prepared by a previously reported procedure[1]; the small amount of free phosphine was removed with a 30% aqueous solution of HCOOH at 0–10°.

The hexane used as solvent was distilled over sodium–potassium alloy under nitrogen. Pure grade cyclohexane (Schuchardt, München) was boiled over sodium–potassium alloy and distilled under nitrogen immediately before use. Commercial tributylphosphine (Fluka) was distilled under nitrogen.

Hydrogenations were carried out in a 250 ml stainless steel swinging apparatus, which could be adjusted to operate at constant pressure (±1 atm) between 10 and 40 atm and at constant temperature (±1°) between 100 and 150°. The pressure and temperature were monitored with a manometer and a thermometer. The temperature was maintained by immersing the autoclave in a thermostatted bath. The catalyst, part of the solvent, and 10 atm of hydrogen were initially fed into the apparatus after evacuation (10^{-3} mmHg residual pressure), while the olefin, and the residual part of the solvent and hydrogen, all contained together in another heated stainless steel vessel, were introduced after the thermostatted bath had reached the required temperature. This was assumed to be the initial time ($t=0$). No induction period was observed except in the case of experiments carried out in the presence of a large excess of phosphine. During the reaction the pressure was maintained constant by feeding hydrogen in through a preheater and a manual valve system. The contributions to the total pressure of the partial pressures of solvent and olefins were taken into account, the relevant values having been previously measured.

The apparatus was adjusted to allow the extracting of samples during the reaction, and these were immediately cooled to $-20°$ and analyzed.

Analytical determinations

VPC analyses were carried out using a C. Erba C–ATC/t apparatus. Cyclohexene–cyclohexane separation was achieved using Carbowax 1500 (25% on silanized Chromosorb 7) with helium as the transport gas (copper column 2 m × 4 mm). For each experiment, the degree of conversion was plotted against time (*e.g.*, Fig. 1), and the initial rate was obtained from the graphical tangent at the origin.

Data were reproducible to within ±5%. No change of the rate was observed on increasing the frequency of the oscillations of the hydrogenation apparatus, even at the highest rates of hydrogenation.

Hydrogen solubility

In Fig. 9 are shown solubility data for H_2 in hexane, obtained using classical solubility methods, under 30 atm pressure. Henry's law was assumed throughout.

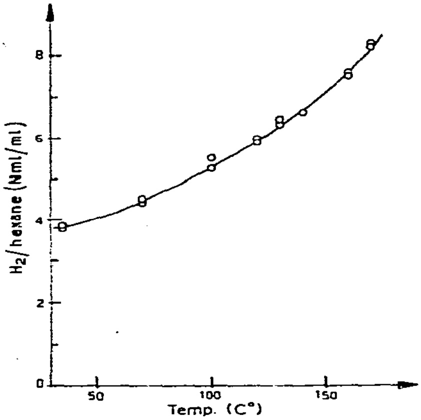

Fig. 9. Hydrogen solubility at different temperatures in hexane at hydrogen partial pressure of 30 atm.

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