# Activation of Hydrogen by Rhodium Complexes Containing Sulphide Ligands. Part III.[1] Studies Involving Substrate Effects and Ligand Effects

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The kinetics are reported for the hydrogenation of *trans*-cinnamic acid and maleic acid using $RhCl_3(Et_2S)_3$ and $RhCl_3[(PhCH_2)_2S]_3$, respectively, as catalysts in *NN'*-dimethylacetamide solution under mild conditions. Ligand-dissociation reactions of rhodium(I)–olefin intermediates appear important and are thought to relieve steric crowding to assist the oxidative addition of *cis*-hydrides. An unusual limiting hydrogenation rate, independent of the total rhodium concentration, is explained by inhibition of the dissociation reaction by sulphide ligands, liberated during formation of the rhodium(I) catalyst.

WE recently[1] described a detailed study of the homogeneous hydrogenation of maleic acid using 1,2,6-$RhCl_3(Et_2S)_3$ in *NN'*-dimethylacetamide (DMA) solution. Further studies using a more bulky olefinic substrate (*trans*-cinnamic acid), and using a rhodium complex with more bulky sulphide ligands (dibenzyl sulphide) have given quite different kinetic dependences for olefin hydrogenation. This paper reports on these findings which show the importance of substrate and ligand effects in dissociation reactions essential to the catalytic process.

## EXPERIMENTAL

The experimental procedure and most of the materials used were described previously.[1] A new complex, trichlorotris(dibenzyl sulphide)rhodium(III), 1,2,6-$RhCl_3(Bz_2S)_3$, was prepared by adding the sulphide (K and K Laboratories) to an ethanolic solution of $RhCl_3,3H_2O$ (Johnson Matthey Ltd.) at room temperature (sulphide: Rh = 3 : 1). The yellow crystalline precipitate obtained on slight warming was washed with ethanol and dried *in vacuo* (Found: C, 59·25; H, 5·05; S, 11·6; Cl, 11·45. $C_{42}H_{42}Cl_3RhS_3$ requires C, 59·3; H, 4·95; S, 11·3; Cl, 11·8%), m.p. 186°. The far-i.r. spectrum showed sharp bands at 317 and 340 $cm^{-1}$ in the region of Rh–Cl modes;[2,3] on comparison with bands at 316 and 344 $cm^{-1}$ which we observed for the $RhCl_3(Et_2S)_3$ complex, which is thought[4] to be the 1,2,6-isomer, the dibenzyl complex is assumed to have the same *trans*-configuration.

## RESULTS AND DISCUSSION

The systems studied were the $RhCl_3(Et_2S)_3$ catalysed hydrogenation of *trans*-cinnamic acid (CA), and the $RhCl_3(Bz_2S)_3$ catalysed hydrogenation of maleic acid.

They were studied as described previously for the maleic acid (MA) system[1] and quite similar gas uptake plots were measured (*cf.* Figure 1 in ref. 1). The initial rates gave the same kinetic dependences, again associated with production of rhodium(I)–olefin complexes; these will not be discussed further, although it should be noted that lower temperatures were employed for the CA system as metal tended to form around 80°, presumably reflecting weaker complexing with the *trans*-olefin.[5]

The linear uptake region in the $RhCl_3(Et_2S)_3$–CA systems showed, however, quite different kinetic dependences to those observed in the MA systems, where first order dependences on rhodium and hydrogen and independences of substrate, added sulphide and added chloride were noted.[1] The hydrogenation was discussed in terms of the following scheme:

$$\begin{tikzcd}
L_3Rh^{I}(\text{olefin}) + H_2 \arrow[r, "\text{slow}"] & L_3Rh^{III}(\text{olefin})H_2 \arrow[d, shift left] \\
L_4Rh^{I} \arrow[u, "\text{olefin}"] & L_4Rh^{III}(\text{alkyl})H \arrow[u, shift left] \arrow[l, "-\text{saturated}", "\text{product}"']
\end{tikzcd}$$

(L = Cl, $Et_2S$, or DMA)

Table 1 summarises kinetic data for the hydrogenation of CA in terms of the linear rates. Figure 1 shows that the rate increases with rhodium at lower concentrations but approaches a constant value at *ca.* 0·015M. The

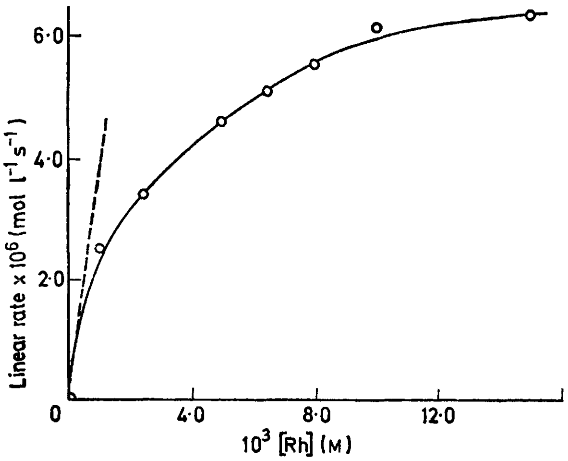

FIGURE 1 $RhCl_3(Et_2S)_3$ catalysed hydrogenation of CA in DMA at 55°. Dependence of linear rate on [Rh]; 0·03M-CA, 1 atm pressure ([$H_2$] = 2·40 × $10^{-3}$M)

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[1] Part II, B. R. James and Miss F. T. T. Ng, *J.C.S. Dalton*, 1972, 355.

[2] R. A. Walton, *J. Chem. Soc.* (*A*), 1967, 1852.

[3] M. A. Bennett, R. J. H. Clark, and D. L. Milne, *Inorg. Chem.*, 1967, **6**, 1647.

[4] J. E. Ferguson, J. D. Karen, and S. Seevaratnam, *J. Chem. Soc.*, 1965, 2627; E. A. Allen, N. P. Johnson, and W. Wilkinson, *Chem. Comm.*, 1971, 804.

[5] M. A. Musks and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

rate is reasonably first order in hydrogen (Figure 2), is independent of CA concentration, and now shows an inverse dependence on both added sulphide and chloride. Salt effects are not significant.[1]

The dependence on rhodium together with the inhibition by $Et_2S$ or LiCl suggests that dissociation of either $Et_2S$ or $Cl^-$ from the $L_3Rh^I(CA)$ complex is now required before the rate-determining reaction with hydrogen:

$$L_3Rh^I(CA) \overset{K}{\rightleftharpoons} L_2Rh^I(CA) + L(=Et_2S \text{ or } Cl^-) \tag{1}$$

$$L_2Rh^I(CA) + H_2 \xrightarrow{k} [L_2Rh^{III}(CA)H_2] \longrightarrow Rh^I + \text{product} \tag{2}$$

The hydrogenation rate is given by:

$$-d[H_2]/dt = kK[Rh][H_2]/(K + [L]) \tag{3}$$

An expression of this form will normally give a limiting half-order in rhodium at higher rhodium concentrations, since with increasing rhodium the [L] term also increases due to the $K$ equilibrium. However, in this system, ligand L is also formed during the production of $L_3Rh^I(CA)$ from the $RhCl_3(Et_2S)_3$ complex.[1] The total [L] will be given by:

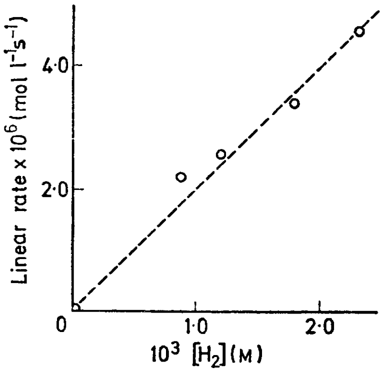

FIGURE 2 $RhCl_3(Et_2S)_3$ catalysed hydrogenation of CA in DMA at 55°. Dependence of linear rate on $[H_2]$; 0·03M-CA, [Rh] = $5 \times 10^{-3}$M

$$[L] = [L_2Rh^I(CA)] + n[Rh] \tag{4}$$

where $n$ is the number of L ligands dissociated in the initial reduction process and is likely to be 1 or 2. Since

$$K = \frac{[L_2Rh^I(CA)][L]}{[Rh] - [L_2Rh^I(CA)]} \tag{5}$$

[L] can be expressed in terms of $K$ and [Rh] by solving equations (4) and (5), and substitution into equation (3) gives the hydrogenation rate, $-d[H_2]/dt$, as

$$\frac{2kK[Rh][H_2]}{K + n[Rh] + \{K^2 + 2(n+2)K[Rh] + n^2[Rh]^2\}^{\frac{1}{2}}} \tag{6}$$

At very low [Rh] ($\ll K$) the rate approximates to $k[Rh][H_2]$, while at very high [Rh] ($\gg K$) the rate becomes $kK[H_2]/n$. The observed rhodium dependence illustrated in Figure 1 is thus consistent with the mechanism of equations 1 and 2 which accounts for the limiting rate zero order in metal. This limiting rate gives $kK/n$ as $2{\cdot}6 \times 10^{-3}$ s$^{-1}$ and the initial slope drawn in Figure 1 suggests a minimum $k$ value of 1·5 l mol$^{-1}$ s$^{-1}$; these data give $K \lesssim n(1{\cdot}7 \times 10^{-3})$ mol l$^{-1}$.

The chloride-dependence data are not too consistent with the dissociated ligand in reaction (1) being chloride. This is readily seen by a consideration of equation (3) which predicts a linear relationship between (rate)$^{-1}$ and [L] and a limiting rate with added chloride as observed (Table 1) is not possible; calculation of individual rates according to equation (3), assuming $n = 1$ (the optimum case) and $K = 1{\cdot}7 \times 10^{-3}$ mol l$^{-1}$, gives the values given in parentheses in Table 1, which are reasonable except in the case for 0·05M added chloride. The same calculation for the single datum at 0·05M added $Et_2S$ gives an estimated rate of $0{\cdot}55 \times 10^{-6}$ mol l$^{-1}$ s$^{-1}$ which is in reasonable agreement with the experimental value of $0{\cdot}40 \times 10^{-6}$ mol l$^{-1}$ s$^{-1}$. We tend to favour dissociation of the $Et_2S$ ligand (see below also) and attribute the inverse chloride dependence to formation of less reactive higher chloro-complexes; $n$ appears to be unity which indicates that reaction (1) involves dissociation from $RhCl(Et_2S)_2(CA)$.

TABLE 1

Kinetic data for the catalysed hydrogenation of *trans*-cinnamic acid using $RhCl_3(Et_2S)_3$ in DMA at 55° unless noted otherwise

| $[Rh] \times 10^3$ (M) | $[H_2] \times 10^3$ (M) | $[CA] \times 10^2$ (M) | Linear rate $\times 10^6$ (mol l$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| 1·0 | 2·40 | 3·0 | 2·48 |
| 2·5 | 2·40 | 3·0 | 3·40 |
| 5·0 | 2·40 | 3·0 | 4·60 |
| 6·5 | 2·40 | 3·0 | 5·08 |
| 8·0 | 2·40 | 3·0 | 5·52 |
| 10·0 | 2·40 | 3·0 | 6·16 |
| 15·0 | 2·40 | 3·0 | 6·32 |
| 5·0 | 2·40 | 6·0 | 4·40 |
| 5·0 | 1·92 | 3·0 | 3·69 |
| 5·0 | 1·28 | 3·0 | 2·60 |
| 5·0 | 0·90 | 3·0 | 2·21 |
| 5·0 | 2·40 | 3·0 | 4·00 [a] |
| 5·0 | 2·40 | 3·0 | 0·40 [b] (0·55) * |
| 5·0 | 2·40 | 3·0 | 3·10 [c] (3·2) * |
| 5·0 | 2·40 | 3·0 | 2·32 [d] (2·5) * |
| 5·0 | 2·40 | 3·0 | 1·60 [e] (1·9) * |
| 5·0 | 2·40 | 3·0 | 1·60 [f] (0·55) * |
| 5·0 | 2·40 | 3·0 | 3·32 [g] |
| 5·0 | 2·39 | 3·0 | 6·48 [h] |
| 5·0 | 2·38 | 3·0 | 8·40 [i] |

* See text.

[a] Using $D_2$. [b] 0·05M-$Et_2S$. [c] 0·0025M-LiCl. [d] 0·005M-LiCl. [e] 0·01M-LiCl. [f] 0·05-MLiCl. [g] 52°. [h] 58°. [i] 61°.

The difference in the kinetic dependences on $Et_2S$ and rhodium in the MA and CA systems arises then from the dissociation reaction shown in equation (1). Such an equilibrium could be involved also for the MA system; if $K$ is large no inhibition by added ligand would be observed, although this seems unlikely since the systems are probably quite similar in terms of electronic ligand effects. However, co-ordinated *trans*-cinnamic acid would give a more sterically crowded complex than the maleic acid, perhaps blocking a prospective co-ordination site, and the oxidative addition step [equation (2)] requires co-ordination of two *cis*-hydrides. In the well known $RhCl(PPh_3)_3$ system,[6-8] dihydride formation to give $H_2RhCl(PPh_3)_2$(solvent) is accompanied by loss of a phosphine ligand, and it seems likely here that dissociation of $Et_2S$ will relieve overcrowding to promote the $H_2$ oxidative addition reaction. Addition of chloride could block a site required by hydride.

The data for the linear hydrogenation rate in the $RhCl_3(Bz_2S)_3$–MA system are summarised in Table 2, and these now parallel the more complex data of the $RhCl_3(Et_2S)_3$–CA system rather than the data for the $RhCl_3(Et_2S)_3$–MA system.[1] The dependence on rhodium (Figure 3) decreases below one with increasing concentration; the rate is first order in hydrogen, independent of maleic acid, and shows an inverse dependence on added dibenzyl sulphide or chloride. The data may be rationalised and analysed as before in terms of equations (1)—(6), except that the co-ordinated ligands involve MA instead of CA, and dibenzyl sulphide instead of diethyl sulphide. The dibenzyl sulphide ligand appears to play the role of the cinnamic acid ligand, and dissociation from the complex is required before the *cis*-dihydride formation occurs; dissociation of the bulky sulphide seems most likely. Cattalini and his co-workers[9] have noted that in $AuCl_3(Bz_2S)$, the sulphide is more labile than chloride, and this was attributed to steric factors.

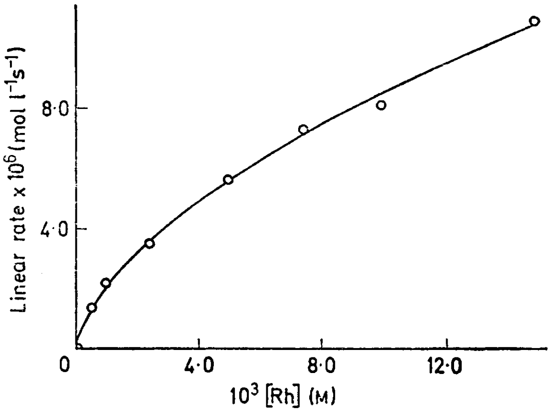

FIGURE 3 $RhCl_3(Bz_2S)_3$ catalysed hydrogenation of MA in DMA at 80°. Dependence of linear rate on [Rh]; 0·03M-CA, 1 atm pressure ($[H_2] = 2{\cdot}32 \times 10^{-3}$M)

The initial slope of Figure 3 gives a *k* value of *ca.* 1·0 l $mol^{-1}$ $s^{-1}$; using this value and equation (3) with the data recorded in Table 2 for added dibenzyl sulphide (assuming sulphide dissociation) gives two values of $K$ both *ca.* $2{\cdot}0 \times 10^{-2}$ mol $l^{-1}$. Thus the limiting rate ($kK[H_2]$), which is reached when $[Rh] \gg K$, is expected to be *ca.* $40 \times 10^{-6}$ mol $l^{-1}$ $s^{-1}$.

The temperature dependence data for the linear rates of Tables 1 and 2 give good Arrhenius plots and activation parameters of $\Delta H^\ddagger = 21{\cdot}3 \pm 1{\cdot}0$ kcal $mol^{-1}$, $\Delta S^\ddagger = 5{\cdot}6 \pm 2{\cdot}0$ e.u. and $\Delta H^\ddagger = 21{\cdot}0 \pm 1{\cdot}0$ kcal $mol^{-1}$, $\Delta S^\ddagger = 0{\cdot}5 \pm 3$ e.u. for the diethyl sulphide and dibenzyl sulphide systems, respectively. Assuming that the rate variation is due principally to changes in *k*, these parameters refer to the hydrogen activation step [equation (2)] and are similar to those determined in the $RhCl_3(Et_2S)_3$–MA system.[1] There was no significant deuterium isotope effect.

TABLE 2

Kinetic data for the catalysed hydrogenation of maleic acid using $RhCl_3(Bz_2S)_3$ in DMA at 80° unless noted otherwise

| $[Rh] \times 10^3$ (M) | $[H_2] \times 10^3$ (M) | $[MA] \times 10^2$ (M) | Linear rate $\times 10^6$ (mol $l^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 0·5 | 2·32 | 3·0 | 1·40 |
| 1·0 | 2·32 | 3·0 | 2·20 |
| 2·5 | 2·32 | 3·0 | 3·42 |
| 5·0 | 2·32 | 3·0 | 5·60 |
| 7·5 | 2·32 | 3·0 | 7·00 |
| 10·0 | 2·32 | 3·0 | 8·00 |
| 15·0 | 2·32 | 6·0 | 10·80 |
| 5·0 | 2·49 | 3·0 | 5·54 |
| 5·0 | 1·70 | 3·0 | 3·66 |
| 5·0 | 0·99 | 3·0 | 2·20 |
| 5·0 | 0·49 | 3·0 | 1·23 |
| 5·0 | 2·32 | 6·0 | 5·62 |
| 5·0 | 2·32 | 3·0 | 5·00[a] |
| 5·0 | 2·32 | 3·0 | 3·00[b] |
| 5·0 | 2·32 | 3·0 | 1·76[c] |
| 5·0 | 2·32 | 3·0 | 4·17[d] |
| 5·0 | 2·32 | 3·0 | 2·20[e] |
| 5·0 | 2·36 | 3·0 | 1·92[f] |
| 5·0 | 2·34 | 3·0 | 3·04[g] |
| 5·0 | 2·30 | 3·0 | 7·36[h] |
| 5·0 | 2·25 | 3·0 | 12·20[i] |

[a] Using $D_2$. [b] 0·05M-BzS. [c] 0·10M-$Bz_2S$. [d] 0·005M-LiCl. [e] 0·045M-LiCl. [f] 70°. [g] 75°. [h] 85°. [i] 90°.

It is of interest to note that the rhodium(I)–dibenzyl sulphide catalyst system could not be used for the reduction of cinnamic acid; even at lower temperatures around 50°, hydrogen treatment readily yielded metal. Steric reasons involving the bulky sulphide ligands and the *trans*-olefin presumably make stabilisation of the rhodium(I) state by olefin complexation difficult. The rhodium(III)–sulphur complexes, unlike corresponding phosphine ones, are readily reduced to the metal by hydrogen and require a further stabilising $\pi$-acid olefin ligand to maintain the rhodium(I) state.

In summary, these kinetic studies indicate the importance of steric effects of catalyst ligands in determining the reactivity of the metal centre towards hydrogen; in the presence of bulky ligands, which can include the olefinic substrate itself, dissociation may be required so that *cis*-dihydride formation can occur. A related reversible ligand dissociation has been demonstrated

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[6] C. O'Connor and G. Wilkinson, *Tetrahedron Letters*, 1969, 1375, and references therein.

[7] R. S. Coffey, 'Recent Advances in Homogeneous Hydrogenation of Carbon–Carbon Multiple Bonds,' in R. Ugo, ed., 'Aspects of Homogeneous Catalysis,' Carlo Manfredi, Milan, 1970, vol. 1, p. 3.

[8] B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, in the press.

[9] L. Cattalini, G. Maragoni, and M. Martelli, *Inorg. Chem.*, 1968, **7**, 1145.

for $RhClL_3$ (L = tertiary phosphines), although in this case the dihydride is already formed and co-ordination of the substrate is inhibited:[10]

$$\underset{\text{active}}{H_2RhClL_2} + L \rightleftharpoons \underset{\text{inactive}}{H_2RhClL_3} \qquad (11)$$

Inhibiting steric effects of phosphine ligands, on the activation of hydrogen for dihydride formation by some iridium(I) complexes, have been reported recently by Vaska and Werneke.[11]

Except for a limitation imposed by solubility, the reaching of a limiting rate with increasing 'catalyst concentration' is most unusual, and incidentally provides further indirect evidence, at least in these systems, that rhodium(I) intermediates are involved in catalytic hydrogenation using rhodium(III) complexes, since it is unlikely that catalyst poisoning would occur *via* re-co-ordination of a ligand to a certain valency state metal centre from which the ligand had dissociated previously. The finding and rationalisation of a hydrogenation rate that may become zero order in rhodium are significant, and should be considered when catalysts are formed *in situ* from a metal complex, usually at higher valence and containing 'superfluous' ligands.

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[10] For example, S. Montelatici, A. Van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1054.

[11] L. Vaska and M. F. Werneke, *Trans. New York Acad. Sci.*, 1971, **31**, 70.