

Journal of Organometallic Chemistry, 186 (1980) 271–277
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KINETICS AND MECHANISM OF THE ANCHORING OF $\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2$ TO POLYMER-BOUND PHOSPHINIC LIGANDS

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(Received July 31st, 1979)

Summary

The reaction between $\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2$ and phosphinic ligands anchored on 2 and 4% polystyrene-divinylbenzene has been kinetically studied. The rate depends on the amount of resin and decreases in the presence of a free leaving ligand. The proposed reaction mechanism is compared with that of the corresponding reaction in homogeneous phase. The results indicate that the complex is mainly bi-anchored to the functionalized resin. The observed variations of the rate constants with temperature do not show any effect attributable to mobility of the resin.

Introduction

Cross-linked polystyrene has been widely used as a support for various reacting groups; intra-resin reactions and reactions between supported groups and chemical species in solution have been studied. The reduced mobility of the anchored groups should favour approximation to the condition of "infinite dilution" and evidence for [1,2,3] and against [4,5] such site insulation has been presented. It seems [6] that to approximate the condition of "infinite dilution" it is necessary to use a highly cross-linked resin and a low concentration of supported groups. Studies have been made of polymer-anchored catalysts [7], but they were aimed at obtaining an active catalyst, and so resins with a low degree of cross-linking and a high concentration of supported groups were used. These immobilized homogeneous catalysts present a very complicated picture, and often even the structure of the bound complex is unclear. It has been suggested that the complex $\text{RhBr}(\text{PPh}_3)_3$ is mainly present as monomer on a 20% cross-linked resin but as dimer on a 2% cross-linked polystyrene-divinylbenzene resin [8]. The complex $\text{RhClCO}(\text{PPh}_3)_2$ appears to be bi-anchored on a 2% cross-linked resin in which 10% of the aromatic rings have been

functionalized [4]. Separation between anchoring sites and flexibility of the polymeric chains have been reported to influence the structure of the supported complex [9]. Furthermore, the catalytic activity is influenced by the extent of insulation of polyanchored complexes [10] and by the mobility of the polymer chains [11].

It seemed that a kinetic study of an anchoring reaction might give valuable information, and we report below a study of the reaction between $\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2$ and resin-supported phosphinic ligands. The conditions used were comparable to those employed in the preparation of the supported catalyst; the resins, with 2 and 4% of cross-linking, contained about 17% of functionalized aromatic rings.

Comparison with previous results for the corresponding homogeneous reaction [12] should give also information on the possible difference in reactivity of the free and anchored phosphinic ligands.

Experimental

Polystyrene-divinylbenzene resins with 2 and 4% cross-linked 200–400 mesh were functionalized with $-\text{PPh}_2$ ligands, by published procedures [13]. Elemental analysis of the functionalized resins indicated P contents of 4 and 3.7% for the 2 and 4% resins, respectively. The same method was used also to attach $-\text{AsPh}_2$ ligands. The complexes $\text{RuCl}_3\text{NOL}_2$ were prepared by a published method [12].

A fixed amount of solution (100 ml) containing the complex and, where appropriate, the leaving ligand was used to suspend a known amount of functionalized resin. The mixture was magnetically stirred. Small aliquots of the liquid phase were withdrawn at suitable intervals and concentration of the complex was determined by ultraviolet spectroscopy [12]. Pseudo first-order conditions were employed throughout, the concentration of the complex always being low compared to the amount of anchored phosphinic ligands and of the free leaving ligand, if present. The final absorbance readings were about 0.05. Good linear kinetic plots were always obtained (the correlation coefficient was usually not less than 0.99). Values of the observed rate constants (k_0) are shown in the Tables; the uncertainties indicated are standard deviations.

TABLE 1
KINETIC DATA OBTAINED WITH A FIXED CONCENTRATION OF TRIPHENYLSTIBINE

[complex]	g of resin ^a	[SbPh ₃]	k_0 (sec ⁻¹)
1.38×10^{-4}	0.018	1.42×10^{-3}	3.39×10^{-6}
1.38×10^{-4}	0.018	1.42×10^{-3}	3.82×10^{-6}
1.38×10^{-4}	0.036	1.42×10^{-3}	9.35×10^{-6}
1.38×10^{-4}	0.036	1.42×10^{-3}	9.89×10^{-6}
1.38×10^{-4}	0.054	1.42×10^{-3}	21.7×10^{-6}
1.38×10^{-4}	0.054	1.42×10^{-3}	18.9×10^{-6}
1.38×10^{-4}	0.072	1.42×10^{-3}	23.9×10^{-6}

^a The resin is a 2% cross-linked polystyrene-divinylbenzene with 4% phosphorus. Runs were performed in 100 ml of CH_2Cl_2 at 30°C.

TABLE 2
KINETIC DATA OBTAINED WITH A FIXED AMOUNT OF RESIN

[complex]	g of resin ^a	[SbPh ₃]	k ₀ (sec ⁻¹)
1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	21.7 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	18.9 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	1.84 × 10 ⁻³	13.7 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	2.12 × 10 ⁻³	11.4 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	2.83 × 10 ⁻³	8.62 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	4.26 × 10 ⁻³	5.95 × 10 ⁻⁶

^a The same conditions as for Table 1.

TABLE 3
KINETIC DATA OBTAINED IN ABSENCE OF TRIPHENYLSTIBENE

[complex]	g of resin ^a	k' ₀ (sec ⁻¹)
1.38 × 10 ⁻⁴	0.018	0.47 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.036	3.49 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.054	6.38 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.054	5.70 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.072	13.7 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.144	37.0 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.180	48.2 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.216	63.3 × 10 ⁻⁹
1.38 × 10 ⁻⁴	0.288	82.3 × 10 ⁻⁹

^a The same conditions as for Table 1.

TABLE 4
KINETIC DATA OBTAINED WITH A FIXED CONCENTRATION OF TRIPHENYLSTIBENE

[Complex]	g of resin ^a	[SbPh ₃]	k ₀ (sec ⁻¹)
1.38 × 10 ⁻⁴	0.018	1.41 × 10 ⁻³	2.75 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.036	1.41 × 10 ⁻³	7.08 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.036	1.41 × 10 ⁻³	7.45 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.054	1.41 × 10 ⁻³	9.32 × 10 ⁻⁶
1.38 × 10 ⁻⁴	0.072	1.41 × 10 ⁻³	17.4 × 10 ⁻⁶

^a The resin is a 4% cross-linked polystyrene-divinylbenzene with 3.7% P. Runs were performed in 100 ml CH₂Cl₂ at 30°C.

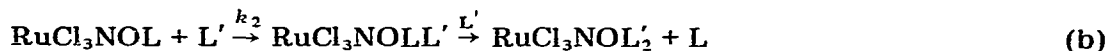
TABLE 5
KINETIC DATA OBTAINED AT DIFFERENT TEMPERATURES

T (°C)	[complex]	g of resin	[SbPh ₃]	k ₀ (sec ⁻¹)
30	1.38 × 10 ⁻⁴	0.054 ^a	1.42 × 10 ⁻³	0.67 × 10 ⁻⁵
40	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	1.33 × 10 ⁻⁵
40	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	1.53 × 10 ⁻⁵
50	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	3.34 × 10 ⁻⁵
50	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	2.67 × 10 ⁻⁵
60	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	6.34 × 10 ⁻⁵
60	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	6.14 × 10 ⁻⁵
30	1.38 × 10 ⁻⁴	0.054 ^b	1.42 × 10 ⁻³	0.32 × 10 ⁻⁵
40	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	0.72 × 10 ⁻⁵
50	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	1.46 × 10 ⁻⁵
60	1.38 × 10 ⁻⁴	0.054	1.42 × 10 ⁻³	2.65 × 10 ⁻⁵

^a 2% cross-linked resin. ^b 4% cross-linked resin. Runs were performed in 100 ml of benzene.

Results and discussion

The following mechanism [12] has been proposed for the homogeneous reaction between complexes of the type $\text{RuCl}_3\text{NOL}_2$ and a phosphinic ligand L' .



The corresponding rate law is:

$$v = k_2 k_1 \frac{[\text{RuCl}_3\text{NOL}_2][\text{L}']}{k_{-1}[\text{L}] + k_2[\text{L}']} \quad (1)$$

The reaction between $\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2$ and resin-supported phosphinic ligands is much slower than the corresponding homogeneous reaction. Even in the pseudo-first order conditions the usual kinetic plots deviated downward, while the initial rate was dependent upon the amount of resin present. These findings are consistent with a much lower value of the rate constant k_2 in eq. 1, which in this case reduces to:

$$v = \frac{k_2 k_1 [\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2][\text{Ph}_2\text{P-Pol}]}{k_{-1}[\text{SbPh}_3]} \quad (2)$$

where the ratio k_1/k_{-1} becomes the equilibrium constant K_e for the first dissociative step (it is assumed that k_1 and k_{-1} retain the same value as in the homogeneous reaction).

Equation 2 is in qualitative agreement with experimental results: it predicts (i) a slower reaction rate (if $k_2 K_e$ is lower than k_1), (ii) a dependence of the rate on the amount of resin, (iii) a retarding effect due to the leaving ligand set free in solution during the reaction. If the leaving ligand is present in large excess with respect to the complex, eq. 2 becomes:

$$v = k_0 [\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2]$$

where

$$k_0 = k_2 K_e \frac{[\text{Ph}_2\text{P-Pol}]}{[\text{SbPh}_3]}$$

Table 1 lists the data obtained for kinetic runs in the presence of a fixed concentration of triphenylstibine; Fig. 1 shows that a linear correlation exists between k_0 and the amount of resin. From the slope it is possible to calculate $k_2 K_e/c$, which turns out to be $(5.79 \pm 0.28) \times 10^{-7} \text{ g l sec}^{-1} \text{ mol}^{-1}$, where c is a conversion factor between the grams of resin and the active concentration of the phosphinic ligands. Table 2 gives the data obtained in presence of a fixed amount of resin and varied concentration of the leaving ligand; the expected linear relation between k_0 and $1/[\text{SbPh}_3]$ is shown in Fig. 2. From this plot a value was calculated for $k_2 K_e/c$ ($(5.76 \pm 0.17) \times 10^{-7}$), in close agreement with that previously found.

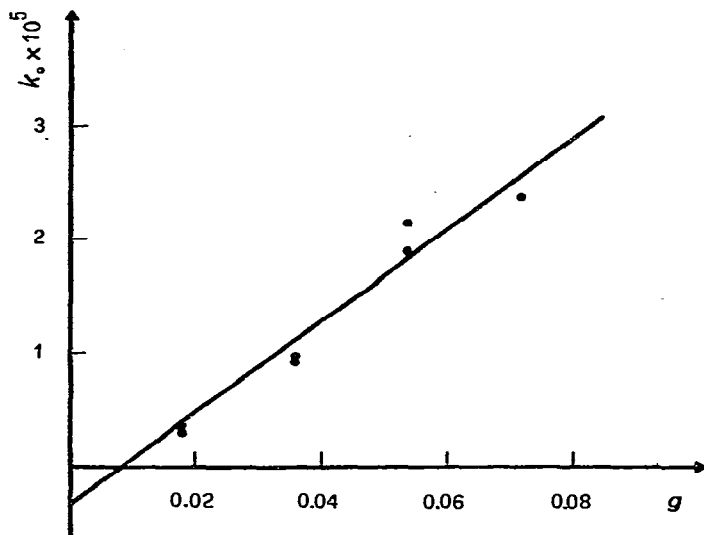


Fig. 1. Plot of k_0 vs. the amount of 2% cross-linked resin: $[\text{SbPh}_3] = 1.42 \times 10^{-3}$.

The remarkable fall in the value of k_z , compared with that in the homogeneous phase can be interpreted in terms of severe steric hindrance around the supported phosphinic ligands. Various factors, such as polymer porosity, pore dimensions, and polymer rigidity, must contribute to such hindrance, which seems to operate also in reactions catalyzed by supported metal complexes [7a]. The integration of eq. 2, with the condition that $[\text{Ph}_2\text{P-Pol}]$ is constant

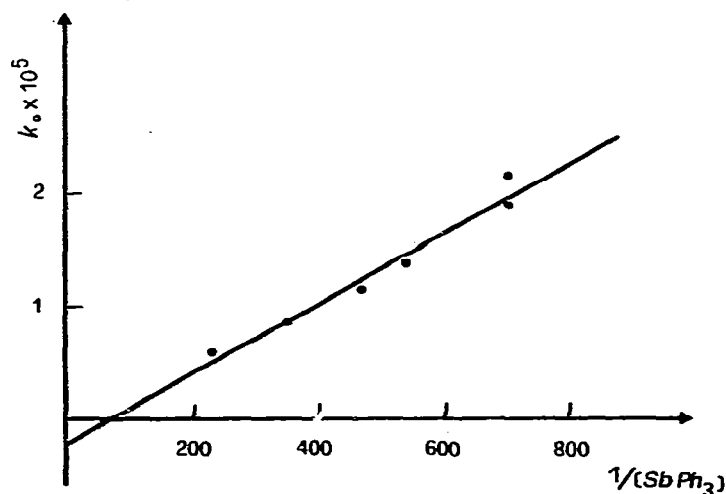


Fig. 2. Plot of k_0 vs. the reciprocal of $[\text{SbPh}_3]$; 0.054 g of 2% cross-linked resin was used.

during a kinetic run, gives

$$\begin{aligned}
 & -[\text{complex}]_0 \ln \frac{[\text{complex}]_t}{[\text{complex}]_0} + [\text{complex}]_t - [\text{complex}]_0 \\
 & = \frac{k_2 K_e}{n} [\text{Ph}_2\text{P-Pol}] \quad (3)
 \end{aligned}$$

where n is the number of molecules of SbPh_3 set free for each molecule of complex leaving the solution, and the subscripts 0 and t refer to time zero and t respectively.

Equation 3 allows another test of the proposed mechanism, in that the left-hand side should be linearly related to t as found experimentally. A plot of the $k'_0 = k_2 K_e/n [\text{Ph}_2\text{P-Pol}]$ values vs. the amount of resin (see Table 3 and Fig. 3), using the previously determined values of $k_2 K_e/c$, permits calculation of n , which turns out to be 1.8. This indicates that there is a strong tendency to chelation, so that the complex is mainly bi-anchored to the polymer. The data obtained for the reaction of $\text{RuCl}_3\text{NO}(\text{SbPh}_3)_2$ and phosphinic ligands supported by a 4% cross-linked resin (see Table 4) are consistent with the proposed mechanism; for this reaction the calculated value of $k_2 K_e/c$ is $(3.60 \pm 0.20) \times 10^{-7}$ which, after correction for the lower phosphorus content, becomes $(3.89 \pm 0.22) \times 10^{-7}$. It appears that in this more rigid resin the proposed intermediate $\text{RuCl}_3\text{NOSbPh}_3$ experiences greater difficulty of access to the phosphinic ligands. This could be due to a variation of k_2 (i.e., increased steric hindrance around the phosphinic ligands) and/or to a variation of $1/c$ (i.e., a larger fraction of the phosphinic ligands unavailable to the substitution reaction).

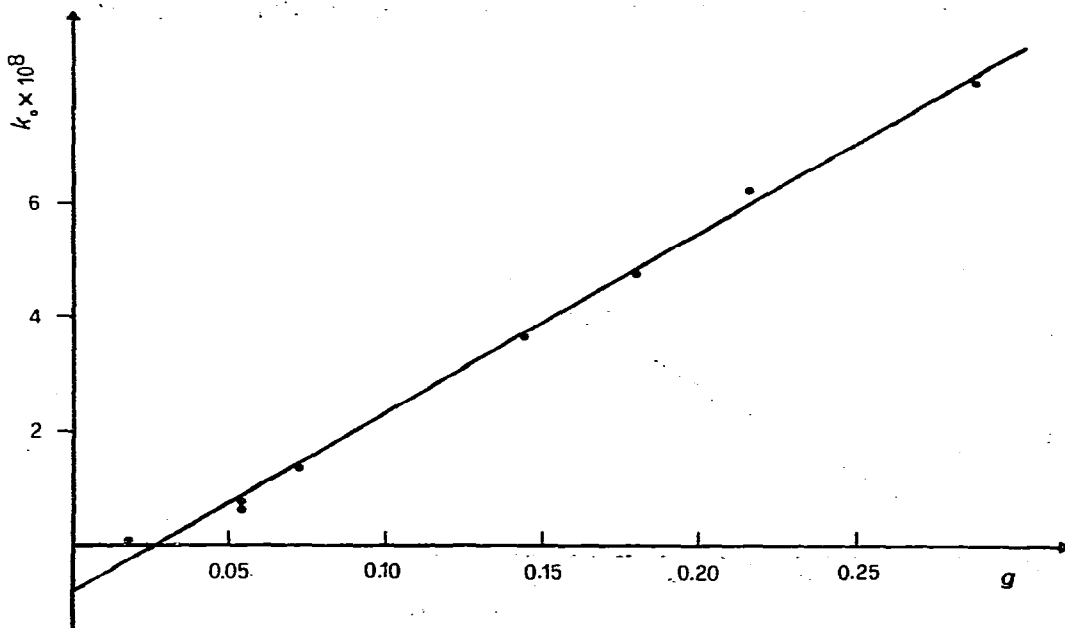


Fig. 3. Plot of k'_0 vs. the amount of 2% cross-linked resin.

The temperature effect on the rate was investigated to examine possible effects connected with the mobility of the polymer chains. To extend the temperature range adequately we changed to benzene as the solvent and the results are reported in Table 5.

At 30°C the rate in benzene is lower than in CH₂Cl₂; the greater swelling of the resin in benzene indicates that the rate reduction is to be associated with a solvent effect on the first dissociative step and/or on k_2 . The $\ln k_0$ vs. $1/T$ plots are linear, so that no definite effect of the resin mobility is observed. The activation energy, inclusive of the ΔH_0 for the first homogeneous dissociative step, is 14.85 ± 0.02 kcal/mol and 14.09 ± 0.01 kcal/mol for the 2 and 4% cross-linked resins respectively.

The strong tendency to chelation found in this anchoring reaction might be common to other systems, so that a decrease of catalytic activity would be expected every time the dissociation of a phosphinic ligand is involved in the catalytic mechanism. However, the use of a large excess of anchored PPh₂ ligands in the present studies might cast some doubt on the suggestion that there is a general preference towards chelation. To clarify this point, we anchored the complex RuCl₃NO(AsPh₃)₂ on a 2% cross-linked resin functionalized with AsPh₂ ligands. This anchored complex does not appreciably react with PPh₃ in solution under the conditions which gave rise to ligand exchange in homogeneous conditions [12]. The hypothesis that this lack of reactivity should be ascribed to the chelation seems to be supported by the very slow reaction, observed in some preliminary runs, between the complex RuCl₃NO-(Ph₂AsCH₂CH₂AsPh₂) and PPh₃ in solution.

Acknowledgement

Financial support from Italian National Research Council is gratefully acknowledged.

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