Polymer-bound Phosphonic Ligands in Substitution Reactions: the Anchoring Mechanism of RhCl$(PPh_3)_3$

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Heterogeneous reactions involving polymer-bound catalysts and chemical species in solution have been widely studied in the last few years [1]. Limitations to the homogeneous phase (with special relevance in the case of catalytic reactions) such as small selectivity, low solubility of the active species and difficulty in their recovery can be overcome by the use of the heterogeneous phase. In our laboratory, kinetic studies on hydrogenation reactions catalyzed by $RhCl(PPh_3)_3$ supported on styrene–divinylbenzene (DVB) resin have been made [2], with particular attention to the role played by the nature of the olefin substrate, the solvent and the polymer.

We also investigated the ligand substitution reaction of $RuCl_3NO(SbPh_3)_2$ in solution with polymer-bound phosphinic ligand [3]. The polymer-bound reagent has been found to decrease the reaction rate with respect to the homogeneous phase [4], allowing the settling of an equilibrium state for the first dissociation step of the Ru complex. This made it possible to study the kinetic effect of the increasing concentration of the leaving ligand during the reaction. The results indicated that the reaction intermediate is the monodissociated complex, and that the anchoring of $RuCl_3NO(SbPh_3)_2$ involves the exchange of both its ligands with those of the polymer.

For the Wilkinson catalyst $RhCl(PPh_3)_3$, complete loss of a phosphinic ligand in solution has been suggested [5], but subsequent data have indicated a much smaller degree of dissociation [6].

We tried to extend the previous kinetic approach to the anchoring of $RhCl(PPh_3)_3$ (10^{-3} *M*) polystyrene–2% DVB resin functionalized with $-PPh_2$ ligands (about 5% in P content). Reactions were carried out under nitrogen in carefully degassed CH_2Cl_2 (20 ml) at 30 °C, and in the presence of an excess of polymer-bound phosphinic ligand (Pol.-PPh_2). Freshly synthesized complex was used, the occurrence of a slow oxidation having been detected by means of mass spectrometry and u.v. spectroscopy. The decrease in the concentration of RhCl$(PPh_3)_3$ has been measured by means of u.v. spectroscopy at 430 nm, recording the spectra from 390 to 450 nm to verify the absence of oxidized complex (see Fig. 1). All the reactions were followed for at least the first 50%.

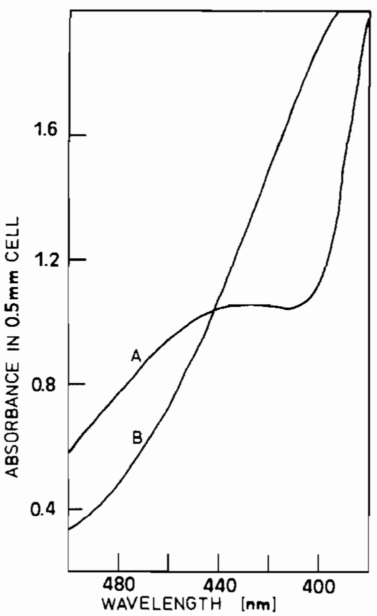

Fig. 1. U.V. spectra of A) $RhCl(PPh_3)_3$ 10^{-3} *M* in CH_2Cl_2; B) the same solution after 1 minute bubbling of oxygen.

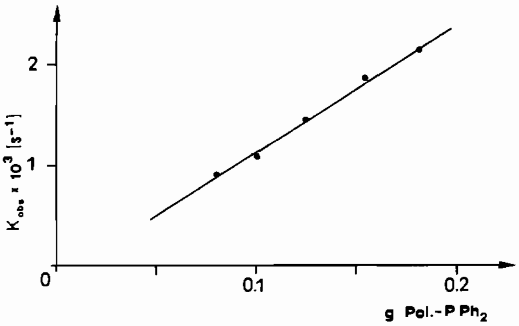

Fig. 2. The effect of the resin amount on the pseudo-first order constant.

At variance with that observed using $RuCl_3NO(SbPh_3)_2$ [3], plots of $\ln[(A_0 - A_{\infty})/(A_t - A_{\infty})]$ *vs.* t were linear, indicating no retarding effect of the leaving ligand on the reaction rate. The observed pseudo-first order kinetic constants (k_{obs}) have been found to be proportional to the excess of functionaliz-

TABLE I. Kinetic Data for the Reaction of $RhCl(PPh_3)_3$ with Polymer-bound -PPh_2 Groups.

g Pol.-PPh_2	$k_{obs} \times 10^3$ [s^{-1}]
0.077	0.88
0.103	1.09
0.125	1.46
0.155	1.86
0.182	2.16

TABLE II. The Effect of Free PPh_3 in Solution on the Reaction of $RhCl(PPh_3)_3$ with Polymer-bound-PPh_2 Groups.

g Pol.-PPh_2	[PPh_3] × 10^3	$k_{obs} \times 10^3$ [s^{-1}]
0.100	5	0.93
0.100	10	1.04
0.100	15	0.95
0.100	20	1.00
0.100	25	1.00
0.100	30	1.00

ed resin (see Table I and Fig. 2). These findings are consistent with a rate equation of the form

$$v = k[\text{Pol.-PPh}_2][\text{RhCl(PPh}_3)_3] \quad (1)$$

A second series of kinetic runs, with constant excess of Pol.-PPh_2 and variable excess of PPh_3 in solution, confirmed that the reaction rate is not dependent on the concentration of PPh_3 (see Table II). Unfortunately this prevents us from gaining information on the number of ligands exchanged by the complex with Pol.-PPh_2 in the anchoring process.

The experimental data indicate that the non-dissociated complex $RhCl(PPh_3)_3$ reacts with the polymer-bound -PPh_2 groups through an associative mechanism, and that its dissociated form $RhCl(PPh_3)_2$ is not kinetically active in this reaction. It might be considered surprising that a dissociated form does not participate in the ligand exchange reaction, since in several cases dissociated complexes, even not detected in solution, have been postulated as reaction intermediates. In the present case, the square planar geometry (even if severaly distorted) of the complex [7], together with a low concentration of the dissociated form, must be responsible for the prevalence of an associative mechanism involving the undissociated complex.

It would be of interest to compare these data with a ligand exchange reaction of $RhCl(PPh_3)_3$ in the homogeneous phase; its reaction with the $P(n\text{-}C_4H_9)_3$ and $Ph_2PCH_2CH_2PPh_2$ ligands, however, is too fast to be followed with normal kinetic techniques, causing an immediate modification of the initial u.v. spectrum.

There is evidence for a strong retarding effect of a polymer-bound ligand on a substitution reaction; since this effect is attributable to steric hindrance, it should be active only in associative steps. This makes the polymer-supported ligands of some use in the study of reaction mechanisms involving associative steps undetectable in the homogeneous phase.

References

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