The Solvent Effect on the Oxidation of Tris(triphenylphosphine)chlororhodium

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Summary The products obtained on oxidation of [$Rh(Ph_3P)_3Cl$] are markedly dependent on the solvent in which the reaction is run.

IT was shown previously that the extent of dissociation of tris(triphenylphosphine)chlororhodium (**1**) by oxygen was solvent dependent.[1] Since an oxidized form of (**1**) has been implicated in the double bond isomerization during olefin hydrogenation[2] over (**1**) and in the rate enhancement of this hydrogenation,[3] the oxidation of (**1**) and related materials in various solvents was investigated.

It has been found that the amount of oxygen reacting with these rhodium complexes during the initial, rapid phase of the reaction was quite solvent dependent. The Table lists the effect of solvent on the amount of oxygen and hydrogen initially taken up by (**1**) and several related compounds.

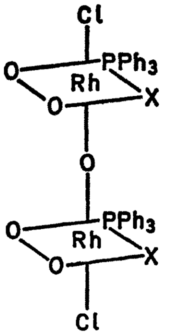
These data indicate that these amounts are quite solvent dependent.

When (**1**) was stirred in air at room temperature and atmospheric pressure 1·75 moles of oxygen were absorbed per mole of (**1**) with a precipitate forming during the reaction. This was filtered and washed thoroughly to remove the triphenylphosphine oxide which was also present. The i.r. spectrum of the residue showed a strong band characteristic of a metal peroxide at 850 cm^{-1}. Complete elemental analysis of the material gave the formula $[Rh_2(Ph_3P)_4Cl_2O_5]$ for which structure (**2**) or a stereoisomer is suggested. The formation of (**2**) by the reaction of 1·75 moles of oxygen with one mole of (**1**) is shown in Equation 1.

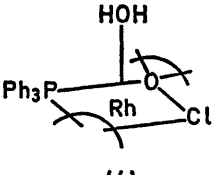
$$2[Rh(Ph_3P)_3Cl] + 3{\cdot}5O_2 \rightarrow [Rh_2(Ph_3P)_4Cl_2O_5] + 2Ph_3P{\rightarrow}O \qquad (1)$$

In ethanol the extensive oxygen uptake by (**1**) (7–20 moles overall) indicated that oxidation of the solvent was also occurring. During the initial, rapid phase of the reaction, however, about three moles of oxygen were absorbed per mole of (**1**) before the rate of absorption slowed markedly. During this time a small amount of a precipitate formed which had a strong i.r. adsorption at 1982 cm^{-1} characteristic of complexed CO. This is further evidence for the formation of acetaldehyde during the reaction.

$[Rh(Ph_3P)_3Cl]$
(1)



(2) X = PPh3
(5) X = C6H6



(4)

Moles of gas reacted per mole of $[RhL_3Cl]$

L	Gas	Benzene	Solvent Methanol	Ethanol
Ph_3P	H_2	1	—	2—3
Ph_3P	O_2	1	1·75	3
$(p\text{-MeO}{\cdot}C_6H_4)_3P$	O_2	1	1·5	—
$(p\text{-Me}{\cdot}C_6H_4)_3P$	O_2	1	—	—
Ph_3As	O_2	1	1·5	6·5

Evaporation of the solution and thorough washing of the residue gave a material which did not show peroxide adsorption bands in the i.r. but did have a strong peak at 1550 cm^{-1} (complexed water). The molecular weight and complete elemental analysis led to the molecular formula $[Rh(H_2O)(Ph_3P)ClO]_{4-5}$ (**3**), presumably a mixture of polymers with the monomeric unit as in (**4**). Assuming that each water molecule arises from the oxidation one of molecule of ethanol, Equation 2 can be used to account for the formation of (**2**) by the uptake of 3 moles of oxygen per mole of (**1**), as observed.

$$[Rh(Ph_3P)_3Cl] + 3O_2 + EtOH \rightarrow [Rh(H_2O)(Ph_3P)ClO] + CO_2 + MeOH + 2Ph_3P{\rightarrow}O \qquad (2)$$

In benzene one mole of oxygen is absorbed very rapidly with another half a mole taken up somewhat more slowly with the reaction almost stopping at that stage. No precipitate was observed. The solution was evaporated and the residue carefully washed giving a species having an i.r. band at 850 cm^{-1} (metal peroxide). Complete elemental analysis and molecular weight determinations led to the assignment of the formula $[Rh_2(Ph_3P)_2Cl_2O_5(C_6H_6)_2]$ to this species. Structure (**5**) is suggested for this material.

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[1] R. L. Augustine and J. F. Van Peppen, preceding Communication.
[2] R. L. Augustine and J. F. Van Peppen, *Chem. Comm.*, 1970, 49.
[3] H. van Bekkum, F. van Rantwijk, and T. van der Putte, *Tetrahedron Letters*, 1969, 1.