

## The Effect of Solvent on the Dissociation of Tris(triphenylphosphine)-chlororhodium

By ROBERT L. AUGUSTINE\* and JAN F. VAN PEPPEN

(Department of Chemistry, Seton Hall University South Orange, New Jersey 07079)

**Summary** The dissociation of  $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$  to  $\text{Ph}_3\text{P}$  and  $[\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}]$  occurs quite readily in benzene but is completely inhibited by the presence of even small amounts of alcohol.

SOLUTIONS of tris(triphenylphosphine)chlororhodium (**1**)  $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$  have been reported to dissociate completely to triphenylphosphine and bis(triphenylphosphine)chlororhodium  $[\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}]$  (**2**) as determined by an osmometric molecular weight determination.<sup>1</sup> On the other hand, n.m.r. data indicated that (**1**) was dissociated only by about 5% in solution.<sup>2</sup> It was felt that the effect which oxygen had on double bond isomerizations during olefin hydrogenations over (**1**)<sup>3</sup> was related to this dissociation problem. Thus, the oxygen and hydrogen promoted dissociations of (**1**) and related compounds were studied in benzene and ethanol. It was found that the presence of triphenylphosphine as well as its oxide in these solutions could be readily monitored by t.l.c.

Benzene solutions of (**1**) when treated with hydrogen or oxygen for a short period of time show the presence of approximately one-third of an equivalent of triphenylphosphine. On similar treatment of  $[\text{Rh}\{(p\text{-MeO-C}_6\text{H}_4)_3\text{P}\}_2\text{Cl}]$  (**3**) with oxygen, almost complete dissociation was observed. Since the dissociated species, (**2**), is considered to be the reactive intermediate in homogeneous hydrogenations involving (**1**)<sup>1</sup> the enhanced dissociation of (**3**) in benzene can be used to account for the more rapid rate of hydrogenation of olefins over (**3**) than over (**1**) in this solvent.<sup>4</sup>

On the other hand the oxygen treatment of ethanol solutions of either (**1**) or (**3**) gave no phosphine; only the phosphine oxide was found. That the oxide did not come from a rapid oxidation of some phosphine which was initially formed by dissociation was shown by the fact that

an excess of phosphine added to the reaction mixture oxidized very slowly.

The ability of ethanol to inhibit dissociation in the presence of oxygen is quite strong since the presence of more than 4% of ethanol in a benzene solution of (**1**) completely stops the dissociation process. However, hydrogenation of benzene-ethanol solutions of (**1**) give triphenylphosphine and  $[\text{Rh}(\text{Ph}_3\text{P})_2\text{H}_2\text{Cl}]$  (**4**) which is apparently quite similar, if not the same, as the dihydride obtained by the hydrogenation of (**1**) in benzene.<sup>1</sup> Whether (**4**) is formed in benzene-ethanol by the addition of hydrogen to a small amount of (**2**) which may be present in equilibrium with (**1**) or by the addition of hydrogen to (**1**) followed by dissociation of the product is uncertain. However, on the basis of the oxidation data, the latter pathway appears to be operative.

These results indicate that not only is the solvent important in the dissociation of species such as (**1**) but also that the lack of dissociation of this complex could well be the cause of olefin isomerization in alcoholic solutions of (**1**). This reaction has been reported to take place even in the absence of hydrogen,<sup>5</sup> something which is quite uncommon for hydrogenation catalysts. The data obtained on the oxygen promoted dissociation of (**1**) in benzene also show that the rate enhancement of olefin hydrogenations over (**1**) which is caused by oxygen is not due to the oxidation of the dissociated phosphine as previously suggested.<sup>6</sup> Instead, it seems probable that this enhancement in rate is due to the reaction of (**2**) with oxygen to give a catalytically more active species. This lack of dissociation in ethanolic solvents also negate the mechanism previously suggested to rationalize the rate and selectivity differences observed in hydrogenation of various substrates over (**1**) in these solvents.<sup>7</sup> It now seems more probable that the suggested "unsaturated route" proceeds through the undissociated (**1**) rather than (**2**).

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