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NON-SELECTIVITY IN THE HOMOGENEOUS HYDROGENATION OF ALKENES USING CHLOROBIS(TRIARYLPHOSPHINE) RHODIUM(I) CATALYSTS

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In the homogeneous hydrogenation of alkenes by $RhCl(PPh_3)_3$ (1-3) the differences in rate between, e.g., alk-1-enes, alk-2-enes and cycloalkenes, arise primarily through the effect of alkene stereochemistry on the formation constant of $RhCl(H_2)(PPh_3)_2$ (alkene). Since the rate of hydrogenation is sensitive to the nature of the phosphine there was reason to check whether the nature of the ligand had an appreciable effect on the selectivity towards various alkenes.

Rate data for alkenes as a function of the ligand are in the Table. Although the rate is highly dependent on the phosphine, (2,3) there is clearly an insignificant effect on the specificity towards a given alkene. This is reasonable if solvent displacement and complexing by the alkene on the hydrido species is involved. The situation differs for $RhH(CO)(PPh_3)_3$ (4) and $RuClH(PPh_3)_3$ (5) where the high selectivity for alk-1-ene stems from steric inhibition to the formation of an intermediate alkyl. The lack of selectivity in the present case does not, of course, necessarily rule out two rapid successive hydrogen transfers via alkyl intermediates as an alternative to simultaneous transfer (1) since such transfers must occur between cis sites which are not mutually cis to two trans phosphines as in the other catalysts (4,5). Indeed n.m.r. spectra of all the hydrido species are consistent with cis PR_3 groups in solvated $RhClH_2(PR_3)_2$ (1-3).

While the tris triphenylarsine and stibine complexes are virtually inactive (6), the bis complexes are quite efficient indicating again the importance of the re-association in the hydrido species (3). The trivial effect of small amounts of oxygen on $RhCl(PPh_3)_3$ (7) is due to removal of the excess phosphine in solution. Although the poisoning effect of excess phosphine was demonstrated previously for cyclohexene (3), very similar data are found for hex-1-ene with a maximum rate at PPh_3:Rh ratio slightly over 2. This is doubtless a general phenomenon.

Table Hydrogenation[a] of alkenes[b]. Relative rates of hydrogen uptake in ml $min.^{-1}$ at 50 cm. partial pressure H_2 and 25°. Catalyst 1.25 mM, substrate 0.6 M, in benzene.

Phosphine Ligand	Hex-1-ene	Cyclohexene	cis-4-Methyl-pent-2-ene	trans-4-Methyl pent-2-ene
tri-p-methoxyphenyl	99.5	68.0	34.7	8.23
tri-p-methylphenyl	85.3	58.8	29.0	6.85
triphenyl	38.9	28.1	14.1	3.12
ethyl diphenyl	17.5			
tri-p-fluorophenyl	5.78	3.93	1.75	0.35
tri-p-chlorophenyl	1.58	1.20	0.44	0.10
tri-2-phenylethyl	1.39			
tri-o-methylphenyl	0.11			
tri-2,3-dimethylphenyl	0.12			
tri-2,4,6-trimethylphenyl	0.09			
triphenylphosphite	0.02			
triphenylarsine	4.63			
triphenylstibine	2.59			

(a) For experimental details see references 1 - 4

(b) Catalyst prepared in situ from the octene complex as in ref.3.

Data for hex-1-ene (Figure) for both species shows linear dependence (pseudo first order) except below ca. 0.5 mM. The apparently higher rate here (cf. ref.1) is attributed, as for $RhH(CO)(PPh_3)_3$ (4) to further dissociation to give an even more active catalyst : $RhCl(PPh_3)_2 \rightleftharpoons RhCl(PPh_3) + PPh_3$. Confirmatory molecular weights cannot be obtained however. The observed catalyst concentration dependence is consistent with a rate : $R = k_a [RhCl(PPh_3)] + k_b [RhCl(PPh_3)_2]$ where $k_a > k_b$. The question of why the addition of but one mole of PPh_3 to $Rh_2Cl_2(octene)_4$ does not give a highly active species is probably that a mono alkene monophosphine complex is not very active for reasons discussed previously (1). The linearity up to 5 mM indicates no appreciable association or dimerisation; the kinetics are as before (1). The difference between $RhCl(PPh_3)_2$ and $RhCl(PPh_3)_3$ confirms the poisoning

effect of PPh_3 and that re-association results in loss of activity.

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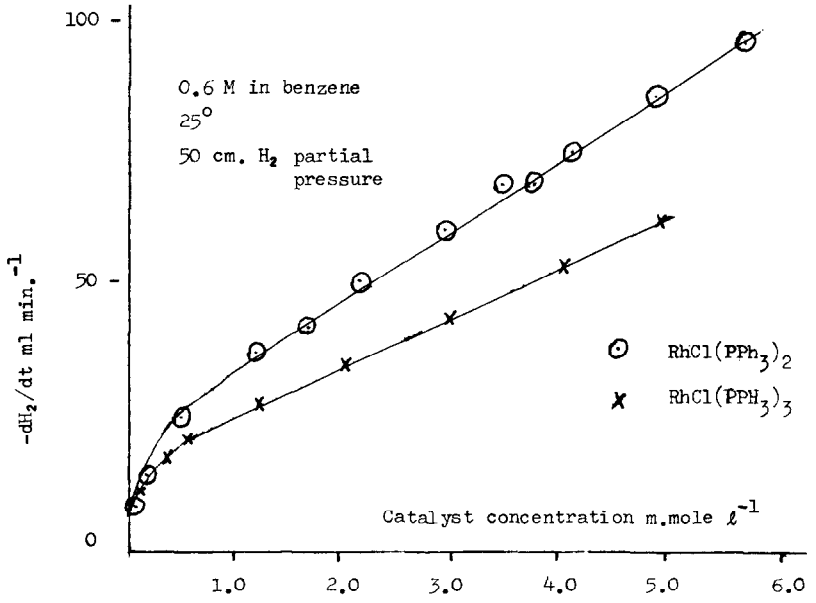

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