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CATALYTIC HYDROFORMYLATION OF UNSATURATED COMPOUNDS USING HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

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Alkenes can be hydroformylated to aldehydes at 25° and 1 atm. using $RhH(CO)(PPh_3)_3$ or similar complexes.(1) Relative rates for several substrates have now been determined (Table) under standard conditions similar to those used for homogeneous hydrogenation.(2) Corresponding rates for gases cannot be compared directly but under similar conditions with 1:1:1 mixtures of alkene, H_2 and CO at 60 cm. total pressure, the uptakes for ethylene and propylene are 4.55 and 1.60 ml.min.$^{-1}$ respectively. No detectable uptake was found for cyclohexene, methyl acrylate, penta-1,3-diene, cycloocta-1,3-diene or α-pinene; hex-1-yne and allyl amine react with the catalyst. Allyl chloride, methallylchloride and vinyl chloride rapidly react giving *trans*-$RhCl(CO)(PPh_3)_2$ and alkene (*cf* CH_3I gives CH_4).

Table Rate in ml.min.$^{-1}$ of CO + H_2 (1:1) absorbed at 50 cm, and 25°.
Catalyst, 2.5 mM; substrate, 1.0 M, in benzene

Substrate	Rate	Substrate	Rate
Allyl alcohol	7.05	Hept-1-ene	3.50
Allyl phenyl ether	5.78	Dodec-1-ene	3.18
Styrene	4.32	Vinyl acetate	0.75
Hexa,1,5-diene	4.26	Cyclooctene	0.26
4-Vinylcyclohexene	4.21	Ethyl vinyl ether	0.20
o-Allylphenol	4.03	Pent-2-enes (*cis* and trans)	0.15
Pent-1-ene[a]	3.74	*cis*-Hept-2-ene	0.12
Allyl cyanide	3.72	*dl*-Limonene	0.10
Allyl benzene	3.56	2-Methyl pent-1-ene	0.06
Hex-1-ene.	3.52		

[a] In *n*-hexaldehyde as solvent, rate = 2.20 ml.min.$^{-1}$

Although the stoichiometric hydroformylation(1) of alk-1-enes gave desirably high yields of straight chain aldehyde, the irreproducibility in the catalytic reactions can be avoided by use of pre-mixed equilibrated gas (British Oxygen Co.Ltd). Under the conditions of the Table, the straight to branched aldehyde ratio is *ca.* 3. However considerable improvements leading to ratios in excess of *ca.* 25 can be made as follows. Hex-1-ene was used as the substrate. (a) The ratio increases linearly with the catalyst concentration. At 25°, 1 atm, H_2 + CO = 1:1, the ratio rises from 3 at 5 mM to 9 at 50 mM catalyst concentration. The low solubility of $RhH(CO)(PPh_3)_3$ is limiting, since the dimer(3), $[Rh(CO)_2(PPh_3)_2]_2$, begins to precipitate at concentrations > 50 mM as the reaction proceeds. However at higher temperatures the solubility is increased and not only the rate but also the product ratio increases. Thus for hexene at 50 mM catalyst, 1 atm. (1:1), the ratio increases from 8.5 (25°) to 13.0 (50°). (b) An increase in the partial pressure of hydrogen (H_2:CO = 2:1) at 15 mM catalyst concentration, 25° and 1 atm. produces an increase to > 25. There is now an increase in the rates of the competitive reactions of isomerisation(2) and hydrogenation(4). (c) The addition of excess triphenylphosphine in 6-fold excess for 30 mM catalyst, 25°, 1:1 gas gives an increase in the ratio from 6.1 to 10.5 although at a substantial sacrifice in rate. However at 40° and 2:1 gas a 3-fold excess markedly suppresses competitive isomerisation(2) and hydrogenation(4). Such solutions remain pale yellow on stopping agitation with gas whereas in absence of excess phosphine the more orange solutions quickly turn red.

It is evident that by adjusting the conditions high ratios can be achieved catalytically; but considering the exceedingly complicated set of reactions involved in the system(1,3,4) no simple interpretation of yields or rates will be possible without detailed study of independent steps.

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