

# Catalysis of Olefin-to-Olefin Addition by Rhodium Chloride

## A NEW HOMOGENEOUS REACTION

Much interest has recently been shown in homogeneously catalysed reactions of olefins. These reactions include isomerisation, polymerisation, hydrogenation, oxidation and carbonylation, and are catalysed with particular efficiency by salts and complexes of rhodium and palladium (1). Their homogeneous performance has the potential advantages over their heterogeneous catalysis of greater selectivity and more economic use of metal atoms. An important development in this field is the reaction recently disclosed by workers in the Du Pont Research Laboratories of olefin self-addition catalysed by rhodium chloride (2, 3). This will be of particular interest in the petrochemical industry as a possible means of upgrading the large quantities of ethylene now or shortly to be available.

Ethylene is dimerised to the equilibrium mixture of *n*-butenes by rhodium chloride in methanol or ethanol at 45° to 150°C with ethylene at atmospheric pressure or above: the presence of the solvent is not essential, and it is believed that the primary product is 1-butene which subsequently is isomerised. Ethylene also combines with propylene to give equal amounts of C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> products, the hydrogenated C<sub>6</sub> fraction containing both *n*-pentane and 2-methylbutane.

The addition of ethylene to butadiene proceeds with great facility with rhodium chloride at 50°C, giving no dimers but chiefly 1,4-hexadiene which is partly isomerised to the 2,4-isomer. The reaction of ethylene with 1,3-pentadiene is even faster, giving 3-methyl-1,4-hexadiene. No doubt a general reaction of considerable importance has been discovered, and many more examples will soon be added to those listed above.

The mechanism of the ethylene dimerisation reaction catalysed by ethanolic solutions of rhodium chloride containing hydrochloric acid has been studied by Cramer (3). An induction period of about 30 minutes is observed, during which time ethylene is absorbed only slowly: the catalytically active species then formed is believed to be the anion  $[(C_2H_4)_2 Rh^I Cl_2]^-$  (A). This ion is also obtained when  $[(C_2H_4)_2 Rh^I Cl]_2$  is dissolved in ethanolic HCl, and when this solution is used as a catalyst no induction period is found.

The ion A is oxidised by HCl to  $[C_2H_1(C_2H_4)Rh^{III}Cl_3 s]^-$  (B) where *s* may be water, ethanol or conceivably Cl<sup>-</sup>. This latter species is of interest because it is the first example of an olefin coordinated to Rh<sup>III</sup>: however at -15°C, where no dimerisation occurs, this ion is unstable and liberates ethylene, and from the solution the salt Cs  $[C_2H_5 Rh Cl_3(H_2O)]$  has been isolated. Dimerisation occurs when the coordinated ethylene molecule in B inserts itself between the ethyl group and the rhodium atom, giving the ion  $[C_4H_6 Rh^{III} Cl_3 s]^-$ : this rapidly loses HCl giving  $[(C_4H_8)Rh^I Cl_2 s]^-$  from which butene and *s* are quickly displaced by ethylene, regenerating the ion A. This is a consequence of ethylene being much more strongly coordinated to Rh<sup>I</sup> than butene. Dimerisation only occurs when the ligands are Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>: other anions and ligands do not allow the reaction to proceed.

### References

- 1 G. C. Bond, *Platinum Metals Rev.*, 1964, **8**, 92
- 2 T. Alderson, E. L. Jenner and R. V. Lindsey, *J. Am. Chem. Soc.*, 1965, **87**, 5638
- 3 R. Cramer, *ibid.*, p. 4717

G. C. B.