Catalysis by Chlorohydridobis(triphenylphosphine)ruthenium(II) Species. Novel Kinetics and Their Implications for Activation of Saturated Hydrocarbons

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Summary Novel kinetics for hydrogenation of acrylamide catalysed by $[\{\mathrm{HRuCl(PPh_3)_2}\}_2]$ in solution indicate a mechanism which includes competitive oxidative addition reactions of H_2 and propionamide (C–H cleavage) to ruthenium(I) centres.

We recently reported isolation of the complexes $[(\mathrm{HRuXL_2})_2]$ ($X = \mathrm{Cl}$ or Br; $L = \mathrm{PPh_3}$ or $\mathrm{AsPh_3}$);[1] the $^{31}P-\{H\}$ n.m.r. spectra of the hydrides and the corresponding $[\{\mathrm{RuX_2L_2}\}_2]$ complexes[1] in C_6D_6 show the AB pattern of a halide-bridged structure with two square pyramids sharing a basal edge.[2]

In attempts to substantiate the involvement[3] of bisphosphine species in catalytic hydrogenations using $[\mathrm{HRuCl(PPh_3)_3}]$, we studied such processes using the isolated hydridobisphosphine dimers. Some unexpected and novel kinetics, and other observations, indicate that the mechanism is as in reactions (1)—(3), which is of special interest in terms of activation of saturated hydrocarbons (the k_{-1} step). Hydrogenations using $[\mathrm{HRuCl(PPh_3)_3}]$ are quite different and involve a rate-determining hydrogenolysis of the ruthenium–alkyl bond.[3]

$$[\mathrm{HRuCl(PPh_3)_2}] + \text{olefin (A)} \overset{K}{\rightleftharpoons} [\mathrm{RuCl(PPh_3)_2\,(alkyl)}] \qquad (1)$$

$$[\mathrm{RuCl(PPh_3)_2(alkyl)}] + [\mathrm{HRuCl(PPh_3)_2}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\{\mathrm{RuCl(PPh_3)_2}\}_2] + \mathrm{AH_2} \qquad (2)$$

$$[\{\mathrm{RuCl(PPh_3)_2}\}_2] + \mathrm{H_2} \xrightarrow{k_2} 2[\mathrm{HRuCl(PPh_3)_2}] \qquad (3)$$

Solutions of $[\{\mathrm{HRuCl(PPh_3)_2}\}_2]$ in dimethylacetamide (*ca.* 10^{-3} M) efficiently catalyse the complete hydrogenation of, for example, acrylamide to propionamide under mild conditions (1 atm H_2, 35 °C); the maximum reaction rates, established after about 10 min, show a second-order dependence on Ru, and a dependence on H_2 that is first order up to *ca.* 100 mmHg and then decreases to approach zero-order at pressures $\geqslant 500$ mmHg. An inverse dependence on acrylamide from 0·01 to 0·8 M, and an inverse dependence on added propionamide at lower H_2 pressures are also observed. The kinetics are most readily interpreted in terms of reactions (1)—(3), which give rate-law (4) on assuming a steady-state treatment for $[\{\mathrm{RuCl(PPh_3)_2}\}_2]$.

$$\frac{-\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = \frac{Kk_1k_2[\mathrm{Ru_{total}}]^2\,[\mathrm{H_2}]\,[\mathrm{A}]}{(1 + K[\mathrm{A}])^2\,(k_2[\mathrm{H_2}] + k_{-1}[\mathrm{AH_2}])} \qquad (4)$$

Analysis of the dependences on Ru, acrylamide, and H_2 indicate a k_1/K value of *ca.* 1·7 s^{-1} at 35 °C, and an independent spectrophotometric study of reaction (1) confirms a 1:1 olefin–hydride reaction with $K = 150$ l $\mathrm{mol^{-1}}$, the hydride being considered a solvated monomer in the strongly co-ordinating solvent. The olefin dependence is reflected in the relative amounts of ruthenium–alkyl and –hydride, and the mechanism predicts a maximum rate when the alkyl and hydride ratio is unity; this requires a free olefin concentration of $1/K$ or *ca.* 7×10^{-3} M. The rates are difficult to measure quantitatively in this concentration range but qualitative agreement is found.

Reactions such as (2) are known[5] for hydrogenations catalysed by $[\mathrm{Co(CN)_5}]^{3-}$, and have been postulated[6] for hydrodimerization of acrylonitrile catalysed by $[\mathrm{RuCl_2(PPh_3)_3}]$. However, we believe the observed kinetics for the present system are unique, and they also give strong evidence for activation of a C–H bond in the propionamide product by what is formally a d^7 $\mathrm{Ru^I}$ dimer; such complexes have been isolated previously from dimethylacetamide solutions.[8]

The k_{-1} and k_2 reactions are oxidative additions of the type well documented for d^7 cobalt(II) systems.[7] Analysis of our kinetic data gives a k_2/k_{-1} value of *ca.* 2000, showing a kinetic preference for H–H over C–H bond cleavage. Oxidative addition of C–H bonds of activated hydrocarbons to d^8 platinum metal systems is known.[9]

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