Thermocatalytic Formation of Molecular Hydrogen and Cyclo-octene from Cyclo-octane by Rhodium Complexes

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Dehydrogenation of cyclo-octane, yielding cyclo-octene and molecular hydrogen, proceeds catalytically with the Wilkinson complex $RhClL_3$ or with its dimeric homologue without photo-irradiation under reflux conditions.

Recently the successful catalytic dehydrogenation of alkanes using transition metal complexes has been achieved, either in the presence of a hydrogen acceptor such as 3,3-dimethylbut-1-ene[1] or under photo-irradiation.[2] Homogeneous alkane dehydrogenation yielding alkene and molecular hydrogen has not been reported previously without photo-irradiation, probably because of its thermodynamic difficulty. Under reflux conditions, however, the dehydrogenation reaction can overcome the equilibrium restriction by separating the product hydrogen from the catalyst solution and from the gas phase in contact with the solution, because these conditions cause the vapour phase to consist exclusively of solvent molecules. Consequently, molecular hydrogen is spontaneously removed from the catalyst solution immediately after its generation.

In this study, we have observed catalytic cyclo-octane dehydrogenation, yielding cyclo-octene and molecular hydrogen, under thermal reaction conditions for the first time using $RhClL_3$ or $[RhClL_2]_2$ [L = PPh_3 and $P(p\text{-tolyl})_3$] complexes.

After treatment with a mixture of conc. H_2SO_4 and HNO_3 to remove unsaturated hydrocarbon impurities, cyclo-octane was dried over $CaCl_2$ and distilled from Na under nitrogen atmosphere. The catalyst complexes were prepared by standard literature methods[3,4] and characterized by ^{31}P NMR spectroscopy (JEOL, FX90Q).

Table 1. Products of cyclo-octane dehydrogenation with $RhClL_3$ and $[RhClL_2]_2$.[a]

Catalyst	H_2/mmol	Cyclo-octene /mmol	Other products /mmol
$RhCl[P(p\text{-tolyl})_3]_3$	2.68	2.85	Toluene (0.33)
$RhCl(PPh_3)_3$	2.38	2.85	Benzene (0.20)
$[RhCl\{P(p\text{-tolyl})_3\}_2]_2$	1.36	1.67	Toluene (0.27)
$[RhCl(PPh_3)_2]_2$	1.27	1.45	Benzene (0.27)
$RhCl(PMePh_2)_3$	0.45	0.49	Methane (trace)
$RhCl(CO)(PPh_3)_2$	0.00	0.00	
$IrCl(CO)(PPh_3)_2$	0.00	0.00	

[a] Catalyst solution: 0.2 mmol metal/100 ml; reaction time: 48 h.

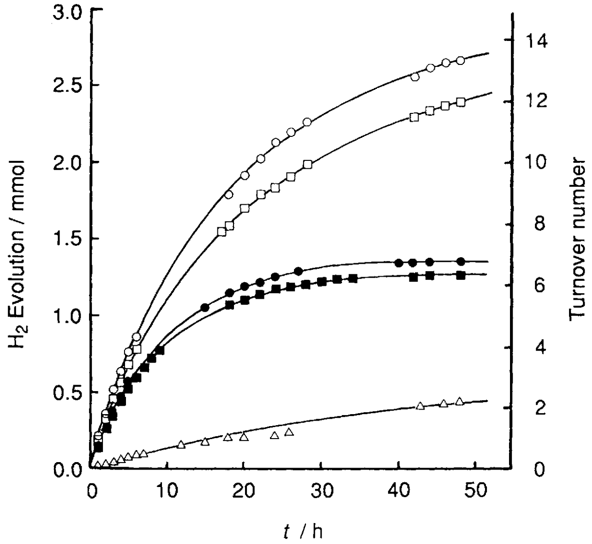

Figure 1. Time-course plots of H_2 evolution from the cyclo-octane solution (0.2 mmol metal/100 ml) of RhCl[P(*p*-tolyl)$_3$]$_3$ (○), RhCl(PPh$_3$)$_3$ (□), [RhCl{P(*p*-tolyl)$_3$}$_2$]$_2$ (●), [RhCl(PPh$_3$)$_2$] (■), and RhCl(PMePh$_2$)$_3$ (△) under boiling and refluxing conditions (151 °C).

All manipulations were carried out under nitrogen atmosphere. The cyclo-octane solution of the complex (0.2 mmol/100 ml) in a Schlenk tube (200 ml) was heated vigorously using an oil bath (180 °C). After the temperature of the solution reached its boiling point (151 °C), the amount of evolved gas was measured by a gas buret (50 ml) through a reflux condenser. GC analysis using an active carbon column showed that the evolved gas consisted exclusively of molecular hydrogen.† The time courses of H_2 evolution are shown in Figure 1. The highest total turnover number of 13.4 after the 48 h reaction was observed for RhCl[P(*p*-tolyl)$_3$]$_3$.

The evolution rates of molecular hydrogen were higher with the Wilkinson type complexes RhClL$_3$ than with their dimeric homologues, whereas RhCl(PMePh$_2$)$_3$ showed a low catalytic activity. A gradual rate decrease accompanied by a darkening of the solution was more distinct for [RhClL$_2$]$_2$ than for RhClL$_3$. Neither the Vaska complex IrCl(CO)(PPh$_3$)$_2$ nor the photocatalytically active RhCl(CO)(PPh$_3$)$_2$ exhibited any reactivity for alkane dehydrogenation under thermal conditions.

The components of the catalyst solution were analysed by GC (OV-1 and PEG-20M capillary columns) after the reaction. The dehydrogenation product proved to be cyclo-octene and no further dehydrogenated products such as cyclo-octadienes were found. Additionally a small amount of toluene or benzene was detected indicating the hydrogenolysis of the phosphine ligand.[5] In fact the stoicheiometric correlation between cyclo-octene and molecular hydrogen was satisfactory, taking the hydrogenolysis into account (Table 1).

The catalyst solution was completely homogeneous in appearance throughout the reaction. The addition of metallic mercury did not affect the reaction rate at all,[6] indicating that no colloidal metal was involved in the dehydrogenation reaction.

The equilibrium $2\mathrm{RhClL}_3 \rightleftharpoons [\mathrm{RhClL}_2]_2 + 2\mathrm{L}$ was ascertained by ^{31}P NMR spectroscopy at room temperature for RhCl[P(*p*-tolyl)$_3$]$_3$ in both cyclo-octane and toluene.[3] After a turnover number of 2.3 was attained, the catalyst solution was characterized again. Most of the RhCl[P(*p*-tolyl)$_3$]$_3$ and [RhCl{P(*p*-tolyl)$_3$}$_2$]$_2$ remained intact, but the free phosphine peak increased to a small extent owing to the partial decomposition of these Rh complexes. Neither alkene nor hydrido complexes were detected.

The effects of free phosphine on the reaction rates were examined by adding P(*p*-tolyl)$_3$ to the cyclo-octane solution of [RhCl{P(*p*-tolyl)$_3$}$_2$]$_2$. The catalyst solutions of [total L]/[Rh] = 2, 3, 8, 15, 30, and 60 gave initial turnover frequencies of 0.89, 1.10, 1.24, 1.15, 0.92, and 0.55 h^{-1}, respectively. A small amount of added phosphine improved the rate while larger amounts inhibited it. A similar tendency was pointed out previously for cyclohexene hydrogenation with the same catalytic system.[3] The concentration of free phosphine affects both the monomer–dimer and the association–dissociation equilibria of the phosphine ligand, which should reflect the reaction rate.

In accordance with thermodynamic circumstances, the co-ordinatively unsaturated species RhClL$_2$ generated from the Wilkinson complex takes a catalytic role for either alkene hydrogenation or alkane dehydrogenation.

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† In addition to molecular hydrogen, a trace amount of methane was detected in the gas evolved from the cyclo-octane solution of [RhCl(PMePh$_2$)$_3$].