Thermocatalytic Dehydrogenation of Alkanes with Wilkinson Complexes

Takahiro Fujii, Yoshifusa Higashino and Yasukazu Saito *
Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Under boiling and refluxing conditions, molecular hydrogen was evolved catalytically, without photoirradiation, from cyclo- and *n*-alkanes using Wilkinson complexes. In the presence of hydrogen acceptors such as alkenes, hydrogen transfer rather than hydrogen evolution occurred. The rates of both reactions using the Wilkinson complex $[RhCl(PR_3)_3]$, R = aryl, were comparable, however, when R = alkyl, the rate of hydrogen evolution was reduced more effectively than that of hydrogen transfer. The mechanisms of the thermocatalytic dehydrogenation of the alkanes using these complexes are discussed in terms of electron-accepting or -donating ligand properties.

The thermal functionalization of alkanes using transition-metal complexes has been one of the most challenging subjects in catalytic chemistry.[1] Hydrogen evolution from alkanes under photoirradiation[2] or hydrogen transfer from alkanes to hydrogen acceptors (*e.g.*, 3,3-dimethylbut-1-ene[3]) has been reported previously, but thermal hydrogen evolution from alkanes under mild conditions has never been attempted, probably because the standard Gibbs free-energy changes are positive in the temperature region lower than the boiling point.

Under boiling and refluxing conditions, however, hydrogen molecules produced in the catalyst solution are separated continuously from the reaction medium and are prevented from the reverse exoergic and exothermic hydrogenation reaction. Thus cyclooctane can be dehydrogenated catalytically using Wilkinson complexes $[RhClL_3]$ [L = PPh_3, $PMePh_2$ or $P(C_6H_4Me\text{-}p)_3$],[4] as well as with supported metals.[5]

In this study, the reaction mechanisms of cyclooctane dehydrogenation with Wilkinson complexes are investigated by comparing the rate of hydrogen evolution with that of hydrogen transfer towards a hydrogen acceptor.

Experimental

In order to remove any unsaturated hydrocarbons, the alkanes were treated with a mixture of concentrated sulfuric and nitric acids, followed by drying over calcium chloride and distillation from sodium under a nitrogen atmosphere. The Wilkinson complexes were prepared by literature methods[6,7] and characterized by ^{31}P NMR spectroscopy using a JEOL FX 90Q spectrometer. All manipulations were carried out under a nitrogen atmosphere. The rate of hydrogen evolution was measured volumetrically; the catalyst solution (2 mmol dm^{-3}) in a Schlenk tube (200 cm^3) was heated to boiling point and refluxed, with the amount of evolved gas measured by a gas burette (50 cm^3). Cyclooctane (19 cm^3) and the alkene (1 cm^3) were treated with the catalyst complex (0.04 mmol metal) under boiling (151 °C) and refluxing conditions for 1 h. The reaction products were then analysed by gas chromatography, using active carbon and GP-54 columns, or OV-1 and PEG-20M capillary columns, for the gas- and liquid-phase components, respectively.

Results and Discussion

Hydrogen Evolution from Cyclooctane.—A cyclooctane solution of $[RhClL_3]$ (L = tertiary phosphine), heated under boiling and refluxing conditions, evolved molecular hydrogen catalytically without photoirradiation (Fig. 1). The Vaska-type complexes $[RhCl(CO)(PPh_3)_2]$ and $[IrCl(CO)(PPh_3)_2]$, known as prominent photocatalysts for alkane dehydrogenation,[2] did not exhibit any thermocatalytic activity.

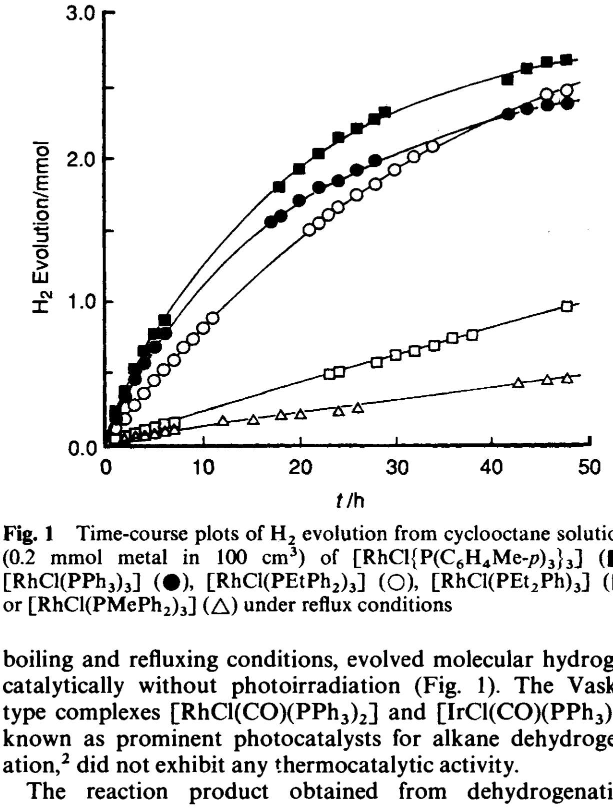


Fig. 1 Time-course plots of H_2 evolution from cyclooctane solutions (0.2 mmol metal in 100 cm^3) of $[RhCl\{P(C_6H_4Me\text{-}p)_3\}_3]$ (■), $[RhCl(PPh_3)_3]$ (●), $[RhCl(PEtPh_2)_3]$ (○), $[RhCl(PEt_2Ph)_3]$ (□) or $[RhCl(PMePh_2)_3]$ (△) under reflux conditions

The reaction product obtained from dehydrogenating cyclooctane in the liquid phase was exclusively cyclooctene. Further dehydrogenated products such as cyclooctadienes were not found. When $[RhCl(PPh_3)_3]$ or $[RhCl\{P(C_6H_4Me\text{-}p)_3\}_3]$ catalysts were used, a small proportion of benzene or toluene, respectively, was also evident, indicating hydrogenolysis of the phosphine ligands.[8] Satisfactory stoichiometric correlation was attained between the molecular hydrogen and the cyclooctene, as far as the hydrogenolysis was concerned (Table 1).

A gradual decrease in the rate of hydrogen evolution was accompanied by a darkening in the solution colour, which was more pronounced for the catalysts co-ordinated with aryl- than with alkyl-substituted phosphines. Moreover, hydrogen evolution from cyclooctane was retarded by adding a small amount of cyclooctene to the solution. Undoubtedly, the gradual rate decrease is caused by product accumulation in the solution in addition to catalyst decomposition. In fact, the hydrogen

Table 1 Products of cyclooctane dehydrogenation using Wilkinson complexes *

Catalyst	Products/mmol H_2	Cyclooctene	Others
[RhCl{P(C_6H_4Me-*p*)$_3$}$_3$]	2.68	2.85	Toluene (0.33)
[RhCl(PPh_3)$_3$]	2.38	2.85	Benzene (0.20)
[RhCl($PMePh_2$)$_3$]	0.45	0.49	Methane (trace)
[RhCl($PEtPh_2$)$_3$]	2.46	2.50	None
[RhCl(PEt_2Ph)$_3$]	0.95	0.93	None

* Catalyst solution, 0.2 mmol metal in 100 cm^3; reaction time, 48 h.

Table 2 Hydrogen evolution from hydrocarbon substrates using [{RhCl[P(C_6H_4Me-*p*)$_3$]$_2$}$_2$] with P(C_6H_4Me-*p*)$_3$ as catalyst

Substrate	*T*/°C	H_2 Evolution/mmol 5 h	24 h	48 h
Cyclooctane	151.0	0.76	2.14	2.68
Cyclohexane	80.7	0.02	0.04	0.05
Decane	174.1	0.25	0.47	0.48
Nonane	150.8	0.08	0.21	0.23
Ethylbenzene *	136.2	0.07	0.12	0.15

* After 72 h 0.20 mmol of H_2 had evolved.

evolution rate (turnover frequency) for [RhCl{P(C_6H_4Me-*p*)$_3$}$_3$] (Fig. 1) decreased from 1.10 to 0.23 h^{-1} after 24 h. On the other hand, the initial rate for the same catalyst was 0.46 h^{-1} when a quantity of cyclooctene, not greater than that formed after the 24 h reaction, was previously added to the solution. These turnover frequency values indicate that the rate decrease was contributed to by both cyclooctene accumulation and catalyst decomposition, neither of which are negligible effects.

The catalyst solution was completely homogeneous in appearance throughout the reaction. Moreover, the reaction rates were utterly unaffected by the addition of metallic mercury to the solution indicating that no colloidal metal was involved in the dehydrogenation reaction.[9]

Hydrogen Evolution from Other Substrates.—Table 2 shows the hydrogen evolution from several hydrocarbon substrates (100 cm^3) at boiling temperatures using [{RhCl[P(C_6H_4Me-*p*)$_3$]$_2$}$_2$] (0.1 mmol) with P(C_6H_4Me-*p*)$_3$ (0.6 mmol) as catalyst.

The higher reactivity by about an order of magnitude of cyclooctane compared with the *n*-alkanes at comparable reaction temperatures is noteworthy. The facile dehydrogenation of cyclooctane may be caused by its rather high ring-strain energy,[10] which leads to its relative instability and a low standard enthalpy change of dehydrogenation (97.4 kJ mol^{-1}). As for ethylbenzene, the turnover number reached 1.0 after reaction for 72 h producing styrene.

Effect of the Phosphine : Rhodium Ratio.—The rates of hydrogen evolution from cyclooctane were affected considerably by the amounts of P(C_6H_4Me-*p*)$_3$ added to the cyclooctane solution of [{RhCl[P(C_6H_4Me-*p*)$_3$]$_2$}$_2$]. As evident from the ^{31}P NMR spectra, a small amount of added phosphine influenced the composition of the catalyst solutions in accordance with equilibrium (1).

$$2\,[\mathrm{RhClL_3}] \rightleftharpoons [\{\mathrm{RhClL_2}\}_2] + 2\,\mathrm{L} \qquad (1)$$

As shown in Fig. 2, the Wilkinson complex of the monomeric type [RhClL_3], favourable at high phosphine concentrations, was more active than its dimeric analogue [{RhClL_2}$_2$], while the reaction rates were retarded by the excess amounts of added phosphine. A similar tendency has been previously[6] observed for the hydrogenation of cyclohexene using the same catalyst system, in which the active species was concluded to be the co-ordinatively-unsaturated species [RhClL_2], generated by the dissociation of a phosphine ligand from [RhClL_3] [equation (2)]. This [RhClL_2] species is therefore proposed as the active species in the dehydrogenation reaction.

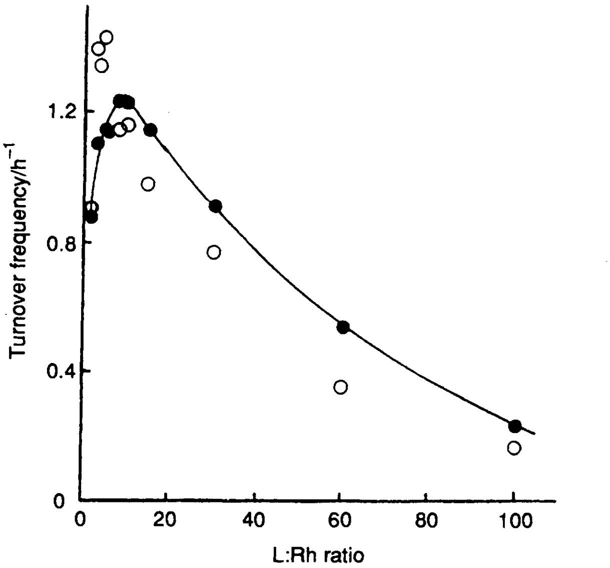


Fig. 2 Rates of hydrogen evolution (●) and hydrogen transfer to non-1-ene (○) from cyclooctane using the catalyst [RhCl{P(C_6H_4Me-*p*)$_3$}$_3$] or [RhCl{P(C_6H_4Me-*p*)$_3$}$_2$]$_2$ (2.0 mmol dm^{-3}) as a function of the phosphine : rhodium ratio

Table 3 Hydrogen transfer from cyclooctane to an alkene under boiling and refluxing conditions using the catalyst [RhCl{P(C_6H_4Me-*p*)$_3$}$_3$]

Alkene	Products (turnover frequency/h^{-1}) Cyclooctene	Alkane
Non-1-ene	1.6	Nonane (1.4)
Cyclododecene	1.5	Cyclododecane (1.6)
Vinylcyclohexane	1.5	Ethylcyclohexane (1.4)

$$[\mathrm{RhClL_3}] \rightleftharpoons [\mathrm{RhClL_2}] + \mathrm{L} \qquad (2)$$

Hydrogen Transfer from Alkane to Alkene.—Hydrogen transfer from alkanes to alkenes [equation (3)] ($\Delta G^\circ \simeq 0$) is

$$\text{alkane} + \text{alkene}' \longrightarrow \text{alkene} + \text{alkane}' \qquad (3)$$

thermodynamically more favourable than the endothermic evolution of hydrogen from the alkane (*e.g.* cyclooctane ⟶ cyclooctene + H_2, ΔG° = 55 kJ mol^{-1}).

Cyclooctane containing non-1-ene (95:5 v/v) was heated with [RhCl{P(C_6H_4Me-*p*)$_3$}$_3$] under refluxing conditions. After the reaction, not only nonane, cyclooctene and a negligible amount of hydrogen were found in the solution, but also isomerized nonenes. When cyclododecene or vinylcyclohexane were used instead of non-1-ene hydrogen transfer from cyclooctane proceeded predominantly (Table 3). Almost equal rates of hydrogen transfer occurred irrespective of the alkene species used and, remarkably, this rate is approximately equal to the rate of hydrogen evolution from the alkene-free cyclooctane.

The rates of hydrogen transfer from cyclooctane to non-1-ene varied with the change (2–100) in the phosphine : rhodium ratio (Fig. 2). A similar dependence and a comparable magnitude of the rates of hydrogen-transfer and -evolution on the phosphine concentration indicates that an active species is common to

Table 4 Catalytic activities of [$RhClL_3$] complexes for the hydrogen transfer from cyclooctane (19 cm^3) to non-1-ene (1 cm^3), the isomerization of non-1-ene to non-2-enes and the hydrogen evolution from cyclooctane not containing any non-1-ene *

	Reaction rate/h^{-1}				Ratio	
L	Nonane	*trans*-Non-2-ene	*cis*-Non-2-ene	H_2	Nonane : H_2	*trans* : *cis*
PPh_3(Cl)	0.99	26.00	11.49	0.69	1.43	2.26
PPh_3(Br)	1.48	52.10	16.26	1.14	1.30	3.20
$P(C_6H_4Me\text{-}p)_3$	1.40	28.13	12.43	1.01	1.39	2.26
$P(CH_2C_6H_4OMe\text{-}p)_3$	1.02	24.08	9.25	0.85	1.20	2.60
$PMePh_2$	0.38	8.31	9.57	0.07	5.85	0.87
$PEtPh_2$	1.00	7.66	12.98	0.50	2.01	0.59
PEt_2Ph	0.45	22.40	37.39	0.13	3.42	0.60

* [Catalyst] = 2.0 mmol dm^{-3}; 151 °C (reflux).

both reactions. The rate of isomerization of non-1-ene, yielding *cis*- and *trans*-non-2-enes also has a comparable dependence on the phosphine concentration. It is quite conceivable that the co-ordinatively-unsaturated species [$RhCl\{P(C_6H_4Me\text{-}p)_3\}_2$], generated thermally from the Wilkinson complex, catalyses all three reactions.

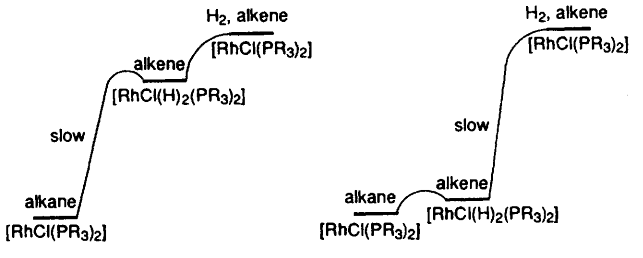
Provided that the catalysis cycle of hydrogen evolution from an alkane is the same cycle, but in the opposite direction to that for alkene hydrogenation,[11] molecular hydrogen would be formed by the reductive elimination of two hydrido ligands from one of the reaction intermediates, *e.g.*, [$RhCl(H)_2\{P(C_6H_4Me\text{-}p)_3\}_2$]. The comparable rates of hydrogen-evolution and -transfer, observed with [$RhCl\{P(C_6H_4Me\text{-}p)_3\}_3$], exclude the possibility that the reductive-elimination step is rate-determining in this catalysis cycle. If it were, the thermodynamically-feasible step of alkene hydrogenation with the dihydride species would proceed much faster than hydrogen evolution. Since cyclooctene is able to accept hydrogen from the dihydride species as well as non-1-ene, the rate decrease of hydrogen evolution during the cyclooctane dehydrogenation is ascribed at least partly to accumulation of product in the solution.

Ligand Effect on the Dehydrogenation.—The initial rates of hydrogen transfer from cyclooctane to non-1-ene (95:5 v/v) present in the solution from the start, the isomerization of non-1-ene to non-2-enes, and the hydrogen evolution from pure cyclooctane are summarized in Table 4 for various Wilkinson complexes. Bromide for chloride substitution in the complex [$RhCl(PPh_3)_3$] improved the rates of both hydrogen evolution and hydrogen transfer to a similar extent (*ca.* 1.5 times), although the rate decrease and the solution darkening became more distinct for [$RhBr(PPh_3)_3$] than for the chloride homologue.

As for the catalysts co-ordinated with aryl-phosphine ligands, similar magnitudes in the rate ratio of hydrogen-evolution to -transfer (1.20–1.43) were obtained. This excludes the rate-determining postulate on the hydrogen elimination step from the dihydride species.

The replacement of any aryl substituent with alkyl in the phosphine ligand generally reduced the rates of hydrogen-evolution and -transfer; a similar tendency was previously reported[12] for catalytic alkene hydrogenation with Wilkinson complexes. The stronger co-ordination of the alkyl phosphines to the metal centre lowers the concentration of the unsaturated active species in these reactions. This strong co-ordination is reflected in the ^{31}P NMR spectrum of the catalyst solution which indicated only a small proportion of liberated phosphine [equation (1)].

The double-bond migration of non-1-ene proceeded much more rapidly than either hydrogen transfer or dehydrogenation. *trans*-Non-2-ene was produced preferentially when the catalyst was co-ordinated with an aryl-phosphine ligand, whereas co-ordination with an alkyl-phosphine ligand gave an increased proportion of the *cis* isomer. As *cis*-non-2-ene is converted to its more stable *trans* isomer,[13] the large *trans*:*cis* ratios for the aryl-phosphine catalysts may be ascribed to the advantageous ligand dissociation, which generates the active species [$RhClL_2$].



(*a*) (*b*)

Fig. 3 Schematic potential profiles of thermocatalytic alkane dehydrogenation with Wilkinson complexes co-ordinated with R = (*a*) aryl- and (*b*) alkyl-substituted phosphine ligands

More remarkable differences between the aryl-substituted and alkyl-substituted phosphine ligands is found in the rate ratio of hydrogen transfer to hydrogen evolution. The high electron-donating capability of the alkyl phosphines stabilizes the dihydride species and suppresses the subsequent reductive-elimination step. Effective rate retardation toward hydrogen evolution will cause the observed high rate ratio (2.01–5.85). As for the Wilkinson complexes co-ordinated with alkyl-substituted ligands, the reductive elimination process, liberating molecular hydrogen, would be rate-determining in the catalysis cycle of cyclooctane dehydrogenation.

The schematic potential profiles of thermocatalytic alkane dehydrogenation with the Wilkinson complexes are depicted in Fig. 3, contrasting the electron-accepting and -donating ligand properties of the aryl- and alkyl-substituted phosphines, respectively.

Conclusion

Under boiling and refluxing conditions, alkanes can be thermocatalytically dehydrogenated using Wilkinson complexes. The reductive-elimination step liberating molecular hydrogen from the dihydride species proceeded easily using catalysts co-ordinated with aryl-phosphine ligands, whereas the alkyl-phosphine ligands suppressed it causing it to become rate-determining in the catalysis cycle.

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