n-Alkene and Dihydrogen Formation from n-Alkanes by Photocatalysis using Carbonyl(chloro)phosphine–Rhodium Complexes

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n-Alkenes and dihydrogen were obtained from n-alkanes by photocatalysis using carbonyl(chloro)phosphine–rhodium complexes; the rate of alkane dehydrogenation was the same as that of propan-2-ol dehydrogenation under the same photocatalytic reaction conditions.

Significant progress has been made in the C–H bond activation of hydrocarbons by transition metal complexes.[1] The formation of stable alkyl and aryl hydride complexes *via* oxidative addition to low-valent complexes[2] and the catalytic dehydrogenation of hydrocarbons *via* hydrogen transfer to an acceptor (3,3-dimethylbut-1-ene)[3,4] have been achieved. However, catalytic formation of an alkene from an alkane accompanied by the evolution of dihydrogen has not so far been reported. We now report that this reaction (1) can proceed at a significant rate under photoirradiation conditions with Vaska-type rhodium complexes [$RhCl(CO)(PR_3)_2$].[5]

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \qquad (1)$$

$$n = 7 \text{ or } 8,\ R = Me, Et \text{ or } Ph$$

Conditions: $h\nu$, $RhCl(CO)(PR_3)_2$

These photocatalytic reactions were carried out in either an internally photoirradiated [light source: high-pressure Hg lamp (400 W, Riko Kagaku)] or an externally photoirradiated apparatus [light source: Xe lamp (2 kW, Ushio)]. Gas evolution was measured by a gas burette, with the components analysed by gas chromatography using an active carbon column. The gaseous product consisted only of dihydrogen; carbon monoxide or other products were not evolved. From n-heptane, both 1- and 2-heptene were identified as products in the liquid phase by co-injection with authentic samples using a capillary column (OV-1, 25 m × 0.25 mm).

Table 1. Photocatalytic dehydrogenation of n-alkanes with Vaska-type rhodium complexes $RhCl(CO)(PR_3)_2$.[a]

R	n-Alkane	T/°C	T.O.F./h^{-1}
Me	Heptane	92	795
Me	Heptane	80	535
Me	Heptane	70	392
Me	Heptane	60	341
Me	Octane	86	650
Me	Octane	70	406
Et	Heptane	80	466
Ph	Heptane	82	136

[a] Catalyst solution: $RhCl(CO)(PR_3)_2$ 3 μmol/200 ml alkane; light source: high-pressure Hg lamp (400 W).

The results obtained with the internal-type photoreactor are summarized in Table 1. The largest turnover frequency (T.O.F.) value of 795 h^{-1} was attained from an n-heptane solution of $RhCl(CO)(PMe_3)_2$ at 92 °C. The temperature dependence was moderate [$E_{act.}$ 23 kJ mol^{-1} for $RhCl(CO)(PMe_3)_2$] and the activity order with respect to the phosphine ligand was $PPh_3 < PEt_3 < PMe_3$. No appreciable difference in rate was found for the reaction of n-heptane and n-octane under the same conditions.

Dihydrogen evolution from the catalyst solution was confirmed by using a UV-34 cut-off filter attached to the external-type photoreactor. The effective wavelength is therefore >340 nm, which includes the metal-to-ligand charge-transfer (M.L.C.T.) band {*trans*-[$RhCl(CO)(PPh_3)_2$], $\lambda_{max.}$ 365 nm}[6] which results in reversible CO dissociation under photoirradiation.[7]

Selective dehydrogenation of propan-2-ol to yield acetone and dihydrogen was studied under the same photocatalytic conditions.[8] It is of particular interest that the rate of alkane dehydrogenation was the same as that for propan-2-ol [$RhCl(CO)(PMe_3)_2$: 535 h^{-1} for n-heptane at 80 °C *vs.* 546 h^{-1} for propan-2-ol at 82.4 °C; $RhCl(CO)(PEt_3)_2$: 466 h^{-1} for n-heptane at 80 °C *vs.* 495 h^{-1} for propan-2-ol at 82.4 °C] and that the activation energies were similar [$E_{act.}$ 22 and 19 kJ mol^{-1} for propan-2-ol with $RhCl(CO)(PEt_3)_2$ and $RhCl(CO)(PEt_2Ph)_2$, respectively].

A quantum yield of 1.6 was found for propan-2-ol dehydrogenation with *trans*-[$RhCl(CO)(PPh_3)_2$].[9] It is apparent that the catalytically active species for this reaction is [$RhCl(PPh_3)_2$] generated by the M.L.C.T. excitation. In this respect, alkanes might be dehydrogenated with a quantum yield higher than unity, since the photoactivation process takes place outside the reactions of the catalytic cycle.

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