ALKENE AND DIHYDROGEN FORMATION BY CATALYTIC DEHYDROGENATION OF ALKANE WITH RhCl(PR₃)₂ PHOTO-GENERATED FROM RhCl(CO)(PR₃)₂

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Summary

Alkene and dihydrogen formation by photocatalytic dehydrogenation of alkanes using RhCl(CO)(PR₃)₂ proceeded with high turnover frequencies, amounting to 1404 h⁻¹ for nonane at 132 °C (PR₃ = PMe₃). The activity order of PPh₃ < PEtPh₂ < PEt₂Ph < PEt₃ < PMe₃ was obtained with respect to the phosphine ligand. Alkane dehydrogenation was retarded by the presence of alkene products, isomerization of which occurred simultaneously. Since dihydrogen was evolved with a first-order rate dependence on photointensities in the 365 nm region, RhCl(PR₃)₂ photogenerated by MLCT excitation was ascribed as the active species in the catalytic cycle of alkane dehydrogenation, which required no further photoassistance. The present one-photon dehydrogenation processes take place with light that is not much higher in energy than some of the C—H bonds that are broken.

Introduction

Dehydrogenation of alkanes by transition metal complexes, yielding alkenes and dihydrogen, is one of the most fascinating goals for organometallic chemistry as well as for catalytic chemistry. Significant progress has been reported recently on the activation of carbon-hydrogen bonds in alkanes with use of low-valent transition metal complexes [1, 2]. Catalytic alkane dehydrogenation was successfully achieved with the aid of 3,3dimethyl-1-butene as a hydrogen acceptor [3] and later without it [4]. Because of the extremely endoergic nature of alkane dehydrogenation, photon assistance was required for reductive elimination from a metal polyhydride complex in a photocatalytic reaction cycle [4, 5]. Burk *et al.* demonstrated clearly the role of the photon in eliminating two hydrido ligands from an iridium complex, which was essentially the same as that of

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the olefinic hydrogen acceptor [4]. Baker and Field also showed that low temperature photoirradiation of an iron dihydride complex in pentane gave dihydrogen and a pentyl iron hydride, which decomposed on warming to afford 1-pentene [5].

Flash-photolysis studies by Wink and Ford gave evidence of photogeneration of a tricoordinate species $RhCl(PPh_3)_2$ under MLCT excitation conditions from $RhCl(CO)(PPh_3)_2$, which was regenerated by rapid coordination of carbon monoxide in a benzene solution [6]. Successful photocatalytic carbonylation with $RhCl(CO)(PPh_3)_2$ was accomplished under a CO atmosphere for benzene [7], which was extended to other hydrocarbons with $RhCl(CO)(PMe_3)_2$ [8].

Recently, remarkable photocatalytic dehydrogenation activities of Vaska-type rhodium complexes $RhCl(CO)(PR_3)_2$ ($PR_3 = t$ -phosphine) were found not only for 2-propanol [9] but also for alkanes [10]. Photocatalytic dehydrogenation rates of 2-propanol and n-alkanes were comparable under similar reaction conditions [10a]. The primary product of n-alkane dehydrogenation was 1-alkene, which isomerized further to internal alkenes [10b].

Catalytic 2-propanol dehydrogenation proceeded with MLCT-photogenerated species $RhCl(PPh_3)_2$ [9a]. Consequently, light is incorporated into photocatalysis by transition metal complexes in two different manners; in one case a reaction intermediate (*e.g.* a metal polyhydride complex) is photoexcited within a catalytic cycle, and in the other a stable catalyst complex (*e.g.* $RhCl(CO)(PR_3)_2$) is photoirradiated to afford the active species (*i.e.* $RhCl(PR_3)_2$) from outside of the catalytic cycle. The role of the photon in alkane dehydrogenation with $RhCl(CO)(PR_3)_2$ at high turnover frequency is elucidated here with emphasis on its incorporation in the catalytic process.

Experimental section

All manipulations were carried out under nitrogen atmosphere. A series of Vaska-type rhodium complexes were prepared by the published methods [11]. Alkanes of reagent grade (Tokyo Kasei Co. Ltd.) were dried and deaerated over Na and benzophenone for more than 24 h by refluxing under N₂ flow. Two types of photoreactors were used; one was a Pyrex glass vessel inserted with a high-pressure mercury lamp (400 W, Riko Kagaku Co. Ltd.) and the other was a cylindrical quartz cell (diameter: 50 mm, cell length: 50 mm) connected to a Xe lamp (2 kW, Ushio Co. Ltd.). The amount of evolved gas was measured by a gas buret through a reflux condenser. The reaction products were analyzed by a gas chromatograph using active carbon and OV-1 capillary (0.25 mm × 50 m, df = 1.5 μ m) columns for the gaseous and liquid phase products, respectively.

Results and discussion

Wavelength dependence of photocatalytic alkane dehydrogenation

Figure 1 shows a time-course plot of evolved gas from the refluxed heptane solution of RhCl(CO)(PMe₃)₂ (10 μ mol/60 ml) with different cutoff filters under photoirradiated conditions. As the sole gaseous product, dihydrogen was evolved at a constant rate with use of a UV-34 cutoff filter; no reaction took place either without photoirradiation or through an L-42 cutoff filter. Similar dependences on these optical filters were observed with RhCl(CO)(PEt₂Ph)₂ and RhCl(CO)(PPh₃)₂ complexes. Since both UV-34 and UV-29 cutoff filters gave the same reaction rates, an effective wavelength was limited to the region of 340 - 420 nm, to which the MLCT bands of these Vaska-type rhodium complexes (*e.g.*, λ_{max} of RhCl(CO)(PPh₃)₂: 365 nm) were included [12]. The MLCT excitation, photogenerating RhCl(PPh₃)₂ from RhCl(CO)(PPh₃)₂, is therefore indispensable to alkane dehydrogenation for these complexes. It is to be noted that RhCl(PR₃)₂ has often been invoked as a key intermediate in catalytic cycles involving Wilkinson-type catalysts RhCl(PR₃)₃ active for alkene hydrogenation [13].

Dihydrogen evolution rates diminished gradually under the reaction conditions^{*}.

Reaction products of photocatalytic alkane dehydrogenation

Product distributions of heptane dehydrogenation using $RhCl(CO)(PMe_3)_2$ complex under internally-photoirradiated conditions are



Fig. 1 Time-course plot for photocatalytic dehydrogenation of heptane with RhCl(CO) (PMe₃)₂ under refluxing conditions with use of cutoff filters

^{*}The gradual decrease in rates was ascribed partly to retardation by the alkene product and partly to catalyst decomposition, accompanied by metallic precipitate formation. Under the externally-photoirradiated conditions with use of the UV-34 cutoff filter, dihydrogen evolution rates were constant at least for 8 h even at refluxing temperatures. Under internally-photoirradiated conditions, however, the rates diminished rather rapidly.

shown in Table 1. The main products were 2-heptenes. Stoichiometric correlations between dihydrogen and total heptenes were sufficiently fulfilled.

Reaction rates of heptane dehydrogenation decreased on adding 1- and *cus*-2-heptenes. As revealed from the amount of 3-heptenes in Table 1, heptene isomerization proceeded from terminal to internal positions. The extents of isomerization were rather suppressed at high reaction temperature and low catalyst concentration, suggesting alkene coordination to the eatalyst complex to be prerequisite for isomerization.

Photocatalytic dehydrogenation of cyclohexane yielded cyclohexene almost exclusively in solution^{*}. Similar product-retardation effects were observed for cyclohexane dehydrogenation by adding cyclohexene. The activity ratio of a cyclohexane/heptane mixture was 2.7, which was larger than that of 1.4 in separate runs (see Table 2)^{**} No formation of coupling products indicated that free or solvent-caged radicals were not involved in the reaction.

Effect of phosphine ligands on photocatalytic alkane dehydrogenation

The initial reaction rates for some alkane substrates are summarized in Table 2 at various reaction temperatures for $RhCl(CO)(PR_3)_2$ (PR₃ = PPh₃, PEtPh₂, PEt₂Ph, PEt₃ and PMe₃). The largest initial turnover frequency of 1404 h⁻¹ was obtained for nonane at 132 °C with $RhCl(CO)(PMe_3)_2$.

Cat. conc. (µmol/ml)	Temp. (°C)	Time (h)	Dıhydrogen		1-Heptene	2-Heptene		3-Heptene	
			mmol	turnovers	(mmol)	cıs	trans	cıs	trans
30/200	92	70	47 6	1587	15	11.1	36.2	tr.	tr
30/150	58	18	19.3	643	tr.	2.9	12.0	5.6	tr.
30/150	60	24	14.9	497	(6.1) ^a	7.9	21.4	6.6	0.4
30/150	60	24	15.1	503	0.3	(18.7) ^b	16.9	6.2	1.7
5/200	68	12	4.2	840	tr.	1.2	2.8	tr.	tr.

Product distribution of photocatalytic heptane dehydrogenation with $RhCl(CO)(PMe_3)_2$ complex^a

^a1-Heptene (a: 27.6 mmol) and *cis*-2-heptene (b: 29.2 mmol) were added before reaction.

*RhCl(CO)(PMe₃)₂ in cyclohexane (5 μ mol/200 ml) yielded dihydrogen (1402 turnovers) and cyclohexene (1289 turnovers) at 68 °C for 3 h.

TABLE 1

^{**}A cyclohexane/heptane (75/75 ml) mixture, reacted with internally photoirradiated RhCl(CO)(PMe₃)₂ (30 μ mol) at 70 °C for 205 h, gave dihydrogen (1393 turnovers), cyclohexene (977 turnovers), cis-2-heptene (50 turnovers), trans-2-heptene (200 turnovers) and cis-3-heptene (117 turnovers). Predominance of cyclohexene to heptenes in the mixture might be attributed to the stability difference between the equilibrated hydrido alkyl complexes, as previously pointed out by Wax *et al* and Buckanan *et al* [2],k] They reported that equilibration of hydrido alkyl complexes was interpreted from the trend of iridium-carbon bond dissociation enthalpies [2k].

TABLE 2

PR ₃	Alkane	Temp. (℃)	T.O.F. (h ⁻¹)
РМез	nonane	132	1404
PMe ₃	nonane	85	619
PMe ₃	octane	86	650
PMe ₃	octane	70	406
PMe ₃	heptane	92	795
PMes	heptane	80	535
PMe ₃	heptane	70	392
PMe ₃	heptane	60	341
PEt ₃	heptane	80	466
PEt ₂ Ph	heptane	83	435
PEtPh ₂	heptane	82	290
PPh ₃	heptane	82	136
PPh ₃	heptane	94	610
PMe ₃	cyclohexane	68	553

Photocatalytic dehydrogenation of alkanes with RhCl(CO)(PR₃)₂^a

^aCatalyst concentration: 3 μ mol/200 ml, except for cyclohexane (5 μ mol/200 ml), light source. high-pressure Hg lamp (400 W).

The effect of phosphine ligands on the photocatalytic rates increased in the order $PPh_3 < PEtPh_2 < PEt_2Ph < PEt_3 < PMe_3^*$. However, the PPh_3 -coordinated complex was more sensitive to the reaction temperature than the others**. The rate order was reversed to $PMe_3 < PPh_3$ at high temperatures. As far as n-alkanes were concerned, the rates were comparable at common reaction conditions irrespective of the chain length but surpassed by cyclohexane.

Photointensity dependence of photocatalytic alkane dehydrogenation

Photointensities at the MLCT region of $RhCl(CO)(PR_3)_2$ complexes were changed by selecting a series of optical filters[†]. As shown in Fig. 2, the dihydrogen evolution rates from the heptane solution of PPh_{3^-} , $PEt_2Ph_{3^-}$ and PMe_3 -coordinated complexes were first order in photointensities in the region around 365 nm. In order for this reaction to proceed only one photon at the MLCT region is therefore required.

^{*}The same ligand effects were obtained previously for 2-propanol dehydrogenation from common complexes [9b]. It is also to be noted that the dehydrogenation rate of alkane was comparable to that of 2-propanol (eg. RhCl(CO)(PMe₃)₂. 535 h⁻¹ at 80 °C for heptane vs 546 h⁻¹ at 82 4 °C for 2-propanol).

^{**}The activation energy of heptane dehydrogenation was determined for RhCl(CO) (PMe₃)₂ as 23 kJ mol⁻¹ from Table 2, which was comparable to that of 2-propanol (22 and 19 kJ mol⁻¹ for RhCl(CO)(PEt₃)₂ and RhCl(CO)(PEt₂Ph)₂, respectively) [9b].

[†]Optical transmittances at 365 nm of the UV-29, UV-34, UVD-36C, UVD-36A and L-42 filters were 92.5, 88.0, 64.5, 52.0 and 0.0% respectively.



Fig. 2. Photointensity dependence on rate of heptane dehydrogenation with RhCl(CO) $(PR_3)_2$. $PR_3 = PPh_3(\Box)$, $PMe_3(\bullet)$ and PEt_2 Ph (\bigcirc).

These results of wavelength and photointensity dependences are important, because MLCT-photogenerated species [6] must be responsible for the catalysis of alkane dehydrogenation without any further photoassistance. In other words, no photon is needed for activating reaction intermediates in the catalytic cycle, even though the themodynamic situation is highly unfavorable (e.g. $\Delta G^0 = 95.1$ kJ mol⁻¹ and $\Delta H^0 = 125.9$ kJ mol⁻¹ for dehydrogenation of heptane to 1-heptene). In the current view on alkane dehydrogenation [4], the thermodynamic driving force for yielding alkene and dihydrogen must be supplemented by a hydrogen acceptor or photoirradiation. However, this thermodynamic difficulty is surmounted under stationarily-photoirradiated conditions, since the catalytically active species is photogenerated at sufficiently high concentration and the reverse reaction is suppressed by the limited amount of dihydrogen dissolved in the solution*.

Photocatalysis previously reported for 2-propanol under the MLCTexcitation of RhCl(CO)(PPh₃)₂ required no incorporation of a photon in the catalytic cycle of dehydrogenation, yielding acetone and dihydrogen in spite of its endoergic and endothermic nature ($\Delta G^0 = 25.02$ kJ mol⁻¹ and $\Delta H^0 =$



Scheme 1

^{*}Under refluxing conditions, the dissolved amount of dihydrogen is actually zero, since no partial pressure is allowed for other substances than the solvent. For this reason, the catalytic cycle of alkane dehydrogenation proceeds without further photoassistance, even though ΔG^0 is large and positive [14].

55.0 kJ mol⁻¹), since the quantum yield exceeded unity ($\Phi = 1.6$ at 108 °C)*.

In this paper, we have demonstrated unequivocally for the first time that dehydrogenation of saturated hydrocarbons is catalyzed by MLCTphotogenerated species from RhCl(CO)(PR₃)₂ without further photoassistance at high turnover frequencies. It should also be noted, in contrast to the case of C—H bond cleavage seen in conventional organic photochemical processes, that the present one-photon dehydrogenation processes are taking place with light (360 nm, 79 kcal einstein⁻¹) that is of not much higher energy than some of the bonds that are being broken.

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^{*}Wavelength and photointensity dependences of 2-propanol dehydrogenation were the same as those obtained for alkane [9b].

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