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PHOTOENHANCED HOMOGENEOUS CATALYTIC HYDROGENATION OF OLEFINS FOLLOWING XeCl EXCIMER LASER EXCITATION OF $RhH(CO)(PPh_3)_3$

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Summary

XeCl excimer laser (308 nm) irradiation of $RhH(CO)(PPh_3)_3$ accelerates the homogeneous hydrogenation of olefins under mild conditions. Significantly enhanced dark reactions were observed after periods of laser irradiation. These demonstrate the generation of a highly active catalytic species. Furthermore, the apparent quantum yield of the reaction has been estimated to be larger than unity (2.4) under appropriate conditions. XeCl excimer laser-induced acceleration of homogeneous hydrogenation with other catalysts, $RhCl(PPh_3)_3$ as well as $IrCl(CO)(PPh_3)_2$ was also observed.

Introduction

Photoexcitation of homogeneous catalysts has been demonstrated to enhance catalytic reactions such as olefin isomerization, hydrogenation, hydrosilation and dehydrogenation over purely thermal reactions. There are many catalytic systems in which UV irradiation has been used to activate metal carbonyl complexes such as $M(CO)_6$ (M = Cr, Mo, W) [1 - 7], $Fe(CO)_5$ [8], metal carbonyl clusters [9], Rh–phosphine [10 - 12] and Ir–phosphine [14, 15] as well as trichlorostannate complexes of rhodium and iridium [16, 17], and Ru–phosphine complexes [18].

Lasers enable the use of strong, monochromatic and coherent light pulses in the field of homogeneous catalysis to activate molecules via their excited states. Recently, it has been reported that excimer laser irradiation of metal carbonyls such as $Fe(CO)_5$ and $Cr(CO)_6$ [19 - 22] produces an active catalyst which has a high turnover frequency and a high quantum yield for 1-pentene isomerization. Furthermore, laser irradiation of $Cr(CO)_6$ and $W(CO)_6$ enhances the water–gas shift reaction [23]. However, thus far

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laser-enhanced catalysis has been restricted to metal carbonyls, $M(CO)_n$. Here, we wish to report an efficient photocatalytic hydrogenation of olefins with $RhH(CO)(PPh_3)_3$ catalyst using a XeCl excimer laser. Significant enhancement of the thermal reaction rate was observed after laser irradiation.

Experimental

The complex $RhH(CO)(PPh_3)_3$ was prepared by published procedures [24 - 26]. Solvents for synthesis of the complex and reaction were used as purchased (GR grade). All experiments and manipulations of compounds were conducted under vacuum or purified N_2, unless otherwise noted.

Photocatalytic hydrogenation by $RhH(CO)(PPh_3)_3$

Typical experiments were performed in an evacuable quartz cell (4 × 1 × 1 cm) equipped with a hydrogen inlet (balloon) and a septum for GC detection at specified intervals. $RhH(CO)(PPh_3)_3$ dissolved in toluene was added to a toluene solution of ethyl acrylate by a syringe, under an H_2 atmosphere. The solution was vigorously stirred. The typical catalyst concentration was 2.0×10^{-3} M and that of ethyl acrylate was 0.8 M in toluene (3.2 ml). The product was analyzed by GC (Shimadzu GC4C; Thermon-1000 (Shimadzu) on 80/100 Chromosorb W; TCD column (4 m)).

General irradiation procedures

A 500 W high pressure Hg lamp, equipped with a UV25 cut-off filter (50% transmittance at 250 nm) and a water filter (10 cm) to remove the UV and thermal spectrum of the irradiated light, was used as a light source. The filtered light was focused to *ca.* 1 cm diameter. Excimer laser irradiation of the reaction solutions was carried out as follows: a XeCl laser beam (*ca.* 8 × 25 mm) from a Lambda Physik excimer laser (Model EMG-103) was used without focusing. The energy was approximately 70 mJ $pulse^{-1}$, and the pulse width was *ca.* 20 ns. The laser-pulse cycle was selected to be 1, 10, or 100 Hz. Total exposure (number of photons irradiated) was measured using a joulemeter (Gentec ED-500).

Results and discussion

$RhH(CO)(PPh_3)_3$ has been found to be one of the most efficient homogeneous hydrogenation [27, 28] and hydroformylation [29 - 31] catalysts. However, under present conditions, the rate of thermal reaction proved slower than reported [24]. Strohmeier *et al.* reported that the catalytic activity was improved by UV irradiation [10], although the details of this photocatalytic behaviour remain unclear.

Figure 1 shows the time course of the catalytic activity as measured by the conversion to ethyl propionate in the homogenous hydrogenation of

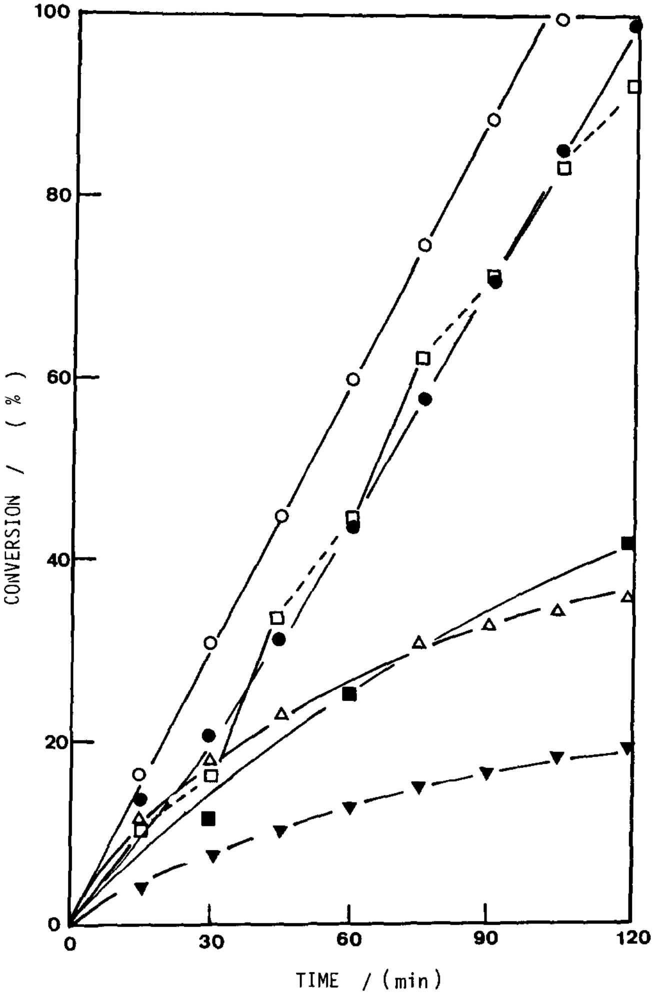

Fig. 1. Time course of hydrogenation of ethyl acrylate with $RhH(CO)(PPh_3)_3$ under thermal, high pressure Hg lamp irradiation, and XeCl laser irradiation (308 nm, 1 Hz); $RhH(CO)(PPh_3)_3$ (2.0×10^{-3} M) and ethyl acrylate (0.8 M) in toluene (3.2 ml). Note the enhanced dark reaction observed during the interval photolysis. (▼) unirradiated reaction at room temperature; (■) under high pressure Hg lamp irradiation; (●) under XeCl laser irradiation (1 Hz); (○) under XeCl laser irradiation (10 Hz); (△) under XeCl laser irradiation (100 Hz); (□) under interval XeCl laser irradiation (1 Hz). (———) irradiated period, (— — —) unirradiated period.

ethyl acrylate with $RhH(CO)(PPh_3)_3$ under thermal and photocatalytic reactions.

$$CH_2{=}CHCOOC_2H_5 + H_2 \xrightarrow[\text{[RhH(CO)(PPh}_3)_3]]{\Delta \text{ or } h\nu} CH_3CH_2COOC_2H_5 \qquad (1)$$

Compared to purely thermal conditions, high pressure Hg lamp irradiation accelerates the rate of hydrogenation. Moreover, XeCl laser irradiation greatly improves this rate. Effective hydrogenation of ethyl acrylate was observed for 1 and 10 Hz irradiation cycles, and the reaction conversion reached 100% within 2 h. The rate of hydrogenation at 100 Hz, however, decreased considerably, almost to that obtained by high pressure Hg lamp irradiation. In this case, the reaction solution contained a precipitate of metallic rhodium. Reduction to rhodium metal was also observed when the solution was irradiated with KrF excimer laser (249 nm) light.

Figure 2 shows the dependence of the rate of hydrogenation of ethyl acrylate on the concentration of the catalyst at a laser cycle of 1 Hz. Note that the reaction rate increases linearly with the increase in catalyst concentration within the region of dilute concentration (*ca.* 1×10^{-3} M). Above this concentration, the irradiated photons are totally absorbed by the reaction solution, as confirmed by absorption spectra. The reaction rate is constant above this concentration when the contribution from the dark reaction, first-order in catalyst concentration, is subtracted.

Table 1 shows selected runs comparing the laser-irradiated hydrogenation reaction with unirradiated and high pressure Hg lamp irradiations. Excimer laser irradiation was found to be superior to Hg lamp irradiation in enhancing hydrogenation, although the number of photons irradiated and absorbed using the laser (70 mJ) was much smaller than that using the Hg lamp (170 mJ). Compared to the activities of Vaska's complex, IrCl(CO)-$(PPh_3)_2$, and Wilkinson's complex, $RhCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$ has proved

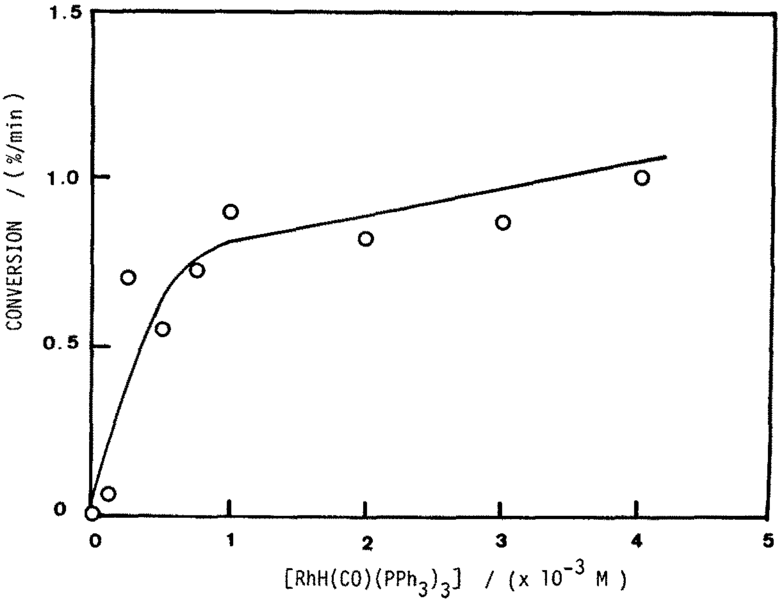

Fig. 2. Dependence of the hydrogenation rate on catalyst solution concentration under XeCl laser irradiation (1 Hz); ethyl acrylate 0.8 M in 3.2 ml toluene solution.

TABLE 1

Excimer laser-induced photocatalytic hydrogenation of olefins

Catalyst precursor [M]	Irradiation[a] conditions (λ(nm)/energy(mJ))	Irradiation frequency (Hz)	Substrate [M]	Solvent (ml)	Product conv. (% h^{-1})
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	L	1	ethyl acrylate (0.8)	toluene (3.2)	43.5 ethyl propionate
$[RhH(CO)(PPh_3)_3 + 10\ PPh_3$ (2.0×10^{-3})	L	1	ethyl acrylate (0.8)	toluene (3.2)	26.1 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	L	10	ethyl acrylate (0.8)	toluene (3.2)	62.2 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	L	100	ethyl acrylate (0.8)	toluene (3.2)	26.7 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	H	—	ethyl acrylate (0.8)	toluene (3.2)	26.2 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	D	—	ethyl acrylate (0.8)	toluene (3.2)	19.3 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.5×10^{-4})	L	1	ethyl acrylate (0.8)	toluene (3.2)	37.5 ethyl propionate
$[RhCl(PPh_3)_3]$ (2.0×10^{-4})	L	1	ethyl acrylate (0.8)	toluene (3.2)	18.3 ethyl propionate
$[IrCl(CO)(PPh_3)_2]$ (5.0×10^{-4})	L	1	ethyl acrylate (0.8)	toluene (3.2)	11.9 ethyl propionate
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	L	1	1-hexene (0.8)	toluene (3.2)	47.7 n-hexane[b]
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	D	—	1-hexene (0.8)	toluene (3.2)	17.9 n-hexane[b]
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	L	1	2-propene-1-ol (0.8)	benzene (3.2)	15.1 n-propanol
$[RhH(CO)(PPh_3)_3]$ (2.0×10^{-3})	D	—	2-propene-1-ol (0.8)	benzene (3.2)	4.0 n-propanol

[a] L = XeCl laser (308 nm) at 70 mJ per pulse; H = filtered high-pressure mercury lamp at 170 mJ per second, see text; D = dark (thermal) reaction at room temperature.

[b] The reaction was retarded after *ca.* 1 h.

to be the best catalyst in our experiments. The quantum yield observed for hydrogenation of ethyl acrylate with $RhH(CO)(PPh_3)_3$ exceeds unity (2.4) following XeCl excimer laser irradiation under appropriate conditions (pulse cycle, 1Hz; catalyst concentration, 1.0×10^{-3} M), which indicates that an active catalyst persists in the dark after photoinitiation in this system*. In fact, we observed other rate enhancement effects during the dark periods after laser irradiation, which again illustrates the production of a long-lived catalyst. There have been few other examples showing dark after-effects following photoactivation, as the enhanced catalysis is often terminated within a few seconds of photoirradiation.

Figure 1 clearly demonstrates that a persistent catalyst was generated by laser irradiation. Similarly, a fairly long-lived active species should be involved in the thermal catalytic cycle. As the role of ligand dissociation in the photocatalysis of transition metal coordination compounds has been well recognized [32], we postulate that the carbonyl ligand of $RhH(CO)(PPh_3)_3$ is photodissociated following laser irradiation (eqn. (2)). CO ligand dissociation from the Vaska-type complexes was recently ascertained by means of flash photolysis [33]. Furthermore, the PPh_3 ligand may be in equilibrium (eqn. (3)) as in other catalytic systems [28 - 30], as the hydrogenation rate was retarded by half on the addition of 10 mol excess PPh_3. Thus, the intermediate '$RhH(PPh_3)_2$' may be involved in the present catalytic hydrogenation with $RhH(CO)(PPh_3)_3$.

$$RhH(CO)(PPh_3)_3 \xrightarrow{h\nu} RhH(PPh_3)_3 + CO \qquad (2)$$

$$RhH(PPh_3)_3 \rightleftarrows RhH(PPh_3)_2 + PPh_3 \qquad (3)$$

As pointed out recently [22], pulsed lasers make it possible to generate coordinatively unsaturated catalytic species at higher concentrations than those produced by high pressure Hg lamp irradiation. Moreover, phosphine dissociation could also be accelerated by irradiation [12]; this could facilitate the generation of coordinatively unsaturated active catalysts. Apparently the laser produces a true catalyst at high concentration, and this is involved in the catalytic cycle, producing the product at high turnover. Thus, the apparent quantum yield, which depends on the lifetime of the intermediate, is greater than unity.

Conclusion

XeCl laser irradiation results in a significant rate enhancement of the homogeneous catalytic hydrogenation of olefins using $RhH(CO)(PPh_3)_3$.

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*The irradiated photons from XeCl laser were totally absorbed by the catalyst solution at this concentration. As any multiphoton process could be neglected, the quantum yield was estimated by dividing the number of product molecules by that of photons irradiated.

The quantum yield for laser irradiation under appropriate conditions was estimated to be greater than unity. Furthermore, enhanced catalytic activity was observed after irradiation. This demonstrates that the photogenerated catalyst by laser sustains its catalytic activity.

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