



A comparative study on photocatalytic hydrogen transfer and catalytic hydrogenation of norbornadiene and quadricyclane catalyzed by $[\text{Rh}_6(\text{CO})_{16}]$

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Abstract

The photo-assisted catalytic transfer hydrogenation and the catalytic hydrogenation of norbornadiene (**I**) and quadricyclane (**II**) over a photo-activated Rh cluster in 2-propanol in the presence of acetone was studied under comparative conditions. With the photo-assisted catalytic transfer hydrogenation, the hydrogen produced by dehydrogenation of 2-propanol is used very effectively for the addition to the reactants without evolving H_2 . Norbornane (**IV**) and nortricyclene (**V**) are formed in parallel in the photo-assisted hydrogen transfer reaction of **II**. In the reaction of **I**, the acetone-sensitized isomerization of **I** to **II** occurs prior to hydrogenation in a concentration of 58 mmol/l of **I**. However, at a lower concentration, we observed a stepwise hydrogenation of **I** to **IV** via norbornene (**III**). The yield of **III** formed in the catalytic hydrogenation was larger than that in the photo-assisted catalytic transfer hydrogenation. Compound **II** was not observed in the catalytic hydrogenation of **I**, and the yield of **V** was less than 1%. Compound **II** behaves in catalytic hydrogenation similar to as in photo-assisted catalytic transfer hydrogenation. The hydrogenation paths of **I** and **II** in both the reactions are discussed on the basis of a reaction mechanism shown in Scheme 1.

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1. Introduction

Previously, the photo-assisted dehydrogenation of alcohols and the evolution of hydrogen gas was reported to occur over metal complex catalysts [1]. Furthermore, the photo-assisted catalytic transfer hydrogenation of di-olefins has been studied over metal carbonyl cluster catalysts [2,3]. However, the com-

parative studies of the hydrogenation of di-olefins have scarcely been investigated over Rh carbonyl cluster catalysts with or without UV-light irradiation. Recently, we reported the photo-assisted selective hydrogenation of limonene by hydrogen transfer from 2-propanol over a Rh carbonyl cluster catalyst $[\text{Rh}_6(\text{CO})_{16}]$ in the presence of a small amount of acetone under UV-light [3]. In the photo-assisted catalytic transfer hydrogenation method, the hydrogen formed by the dehydrogenation of 2-propanol was very efficiently added to unsaturated compounds. In other words, no perceptible dihydrogen was produced

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in the gas phase during this process. We applied this effective process of hydrogen transfer to the hydrogenation of norbornadiene (**I**). No photo-assisted catalytic transfer hydrogenation of **I** and quadricyclane (**II**) over a photo-activated Rh carbonyl cluster catalyst under UV-light irradiation has been studied, although there have been many studies on valence isomerization in the **I–II** system, with respect to solar energy storage [4]. The catalytic hydrogenation of **I** is expected to proceed in two steps through norbornene (**III**) as a stable intermediate to norbornane (**IV**). Thus, the selectivity for partial hydrogenation to **III** constitutes an interesting subject of investigation from the standpoint of photo-assisted catalytic transfer hydrogenation.

In this paper, we would like to report on a detailed comparison with respect to reactivities and the reaction mechanism for photo-assisted catalytic transfer hydrogenation and the catalytic hydrogenation of **I**, **II** and **III**.

2. Experimental

2.1. Materials

Compound **I** of Cica-Reagent Grade was purchased from Kanto Chemicals, Tokyo. This compound in a purity of over 98 mol% as judged by gas chromatography was used without further distillation. Compound **II** was prepared by the photo-reaction of compound **I** according to the method described by Smith [5]. By gas chromatography, the distilled compound **II** was determined to be 96 mol% pure, containing compound **I** (3.5 mol%), and unidentified substance (0.5 mol%). Compound **III** was purchased from Wako Chemicals, Tokyo.

The solvent (2-propanol) and additive (acetone) of Guaranteed Reagent Grade were purchased from Wako Chemicals, Tokyo, but they were used without further purification.

2.2. Catalysts

Hexadecacarbonylhexarhodium $[\text{Rh}_6(\text{CO})_{16}]$ (Rh carbonyl cluster complex) was purchased from Sigma–Aldrich. The Rh metal catalyst was prepared by the method described previously [6].

2.3. Typical photo-assisted catalytic transfer hydrogenation procedure

Prior to the reaction, $[\text{Rh}_6(\text{CO})_{16}]$ (36 mg) as a catalyst precursor was pre-irradiated with a 100 W high pressure mercury lamp at 15 °C for about 30 min for activation in the presence of acetone (3.0 cm³, 40 mmol) as a photo-sensitizer, and 2-propanol (200 cm³) in a quartz reaction vessel under argon. Then **I**, **II** or **III** (about 1.0 cm³ or 1.0 g) was put into the reaction vessel, and then the reaction mixture was stirred magnetically under UV-light irradiation as mentioned above.

2.4. Typical catalytic hydrogenation without UV-light irradiation procedure

The Rh carbonyl cluster complex was activated by the same method as in the photo-assisted catalytic transfer hydrogenation. A quartz reaction vessel containing the activated Rh cluster catalyst in the suspension was charged with hydrogen gas, and then the catalytic hydrogenation was carried out at 30 °C under 1 atm of H₂ after **I**, **II** or **III** (about 1.0 cm³ or 1.0 g) was added to the reaction vessel.

The composition of the reaction mixture in the course of the photo-assisted catalytic transfer hydrogenation or the catalytic hydrogenation without UV-irradiation was analyzed by gas chromatography at certain intervals of time. All products were analyzed by gas chromatography using a CBP-1 capillary column (25 m) heated at 303 K (Shimadzu GC-14B, Shimadzu Co., Tokyo) and also identified by direct comparison with authentic samples. In particular, **V** was confirmed by gas chromatography–mass spectroscopy (JMS-Automass 120, JEOL Ltd., Tokyo). Evolved hydrogen gas was collected using a gas burette.

3. Results and discussion

We expected that the photo-assisted catalytic transfer hydrogenation of **I** would proceed as smoothly as with limonene as reported in our earlier paper [3]. However, the catalytic behavior of the Rh carbonyl cluster complex $[\text{Rh}_6(\text{CO})_{16}]$ in the reaction of **I** is different from that in the reaction of limonene in the

process of the photo-assisted catalytic transfer hydrogenation of **I**. The reproducibility of the catalytic activities were poor in the reaction of **I**, when the Rh carbonyl cluster complex was used without pre-irradiation. We attempted to activate the Rh carbonyl cluster complex in the presence of a small amount of acetone in 2-propanol by UV-irradiation for 30 min just before the addition of the substrates, **I**, **II** or **III**. Consequently, the activated Rh cluster catalyst gave rise to invariably reproducible reactivities for **I**, **II** and **III**. The need of pre-irradiation will be discussed later.

3.1. Photo-assisted catalytic transfer hydrogenation

In this reaction, the activation of the Rh carbonyl cluster complex and the formation of hydrogen from 2-propanol were initiated by 1-hydroxy-1-methylethyl radicals formed in the reaction process, as was discussed in our earlier paper [3]. The 1-hydroxy-1-methylethyl radical is formed through the abstraction of hydrogen from 2-propanol by an excited acetone. The evolution of hydrogen gas took place easily, when the Rh carbonyl cluster complex was activated by UV-light irradiation in the presence of a small amount of acetone in 2-propanol prior to the start of the photo-assisted catalytic transfer hydrogenation of **I**, **II** or **III**. Interestingly, the evolution of the hydrogen gas was stopped immediately by the addition of **I**, **II** or **III** to the reaction vessel. Instead, the photo-assisted catalytic transfer hydrogenation of **I**, **II** and **III** proceeded to give the corresponding products. Fig. 1a and b show the time versus the reaction course on the photo-assisted catalytic transfer hydrogenation of **I** over the photo-activated Rh cluster catalyst. On the photo-assisted catalytic transfer hydrogenation of **I**, we supposed it would proceed via a consecutive reaction such as $\text{I} \rightarrow \text{III} \rightarrow \text{IV}$. However, as can be seen from Fig. 1a, **II** is preferentially obtained at an initial stage of the reaction. This can be explained by that the energy of UV-light is utilized more effectively for the valence isomerization of **I** and **II** than for the transfer to substrates of the hydrogen formed or the formation of hydrogen by the photo-assisted catalytic dehydrogenation of 2-propanol. It has been known that **II** is formed by rapid ring-closure of **I** by means of irradiation of UV-light [4] and also **II** is relatively

stable at room temperature but reverted to **I** when heated to 140 °C [7] or in the presence of transition metal complexes [8]. Therefore, the photo-assisted catalytic transfer hydrogenation of **I** may be achieved under the valence isomerization of alternating **I** and **II**. The photo-assisted catalytic transfer hydrogenation of **I** gradually occurred in the vicinity of the maximum concentration of **II** (about 62%) formed by isomerization of **I**, and then **IV** was produced over the amounts of **III** formation. The hydrogen formed on the activated Rh cluster catalyst seems to add preferentially to **II** formed from **I** rather than to evolve as hydrogen gas (see Fig. 1a). In the consecutive reaction of **I**, there was a small production of stable intermediate **III** (about 8% maximum yield) as can be seen from Fig. 1a. The formation of **III** may be correlated to the extent of the valence isomerization from **I** to **II**.

Nortricyclene (**V**) was produced in about 30% yield in this reaction. As discussed later, **V** is not the product from **I** but from **II**, although it has been known that the catalytic hydrogenation of **I** over $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ complex gave **V** in a yield of 17% as a by-product together with **II** or **III** [9]. The photo-assisted catalytic transfer hydrogenation of **II** is similar to that of **I**, with respect to the formation of **IV** and **V** (Fig. 1b). The formation of **V** from **II** was more remarkable than that from **I**. However, **III** could not be obtained by the photo-assisted catalytic transfer hydrogenation. In this study, our attention was focused on the selectivity for the formation of **III**. Hanaoka et al. have reported [2b] on a photocatalytic transfer hydrogenation of 1,5-cyclooctadiene over a modified Rh colloid catalyst which is obtained from the $[\text{Rh}_4(\text{CO})_{12}]$ complex. Its reaction proceeded successively and the cyclooctene intermediate could be obtained as an intermediate in good yield (over 86% yield). However, the formation of **III** was very small in the reaction of **I** and **II**, as described above. The formation of **III** and **IV** would take place under a mechanism different from the successive reaction presented by Hanaoka et al.

Probably, **I** is hydrogenated mainly via **II**. Assuming an extensive reaction pathway such as Scheme 1 for **I** and **II**, the selectivity on the formation of a stable intermediate **III** in the photo-assisted catalytic transfer hydrogenation of **I** and **II** may be lower than that reported in Hanaoka's work.

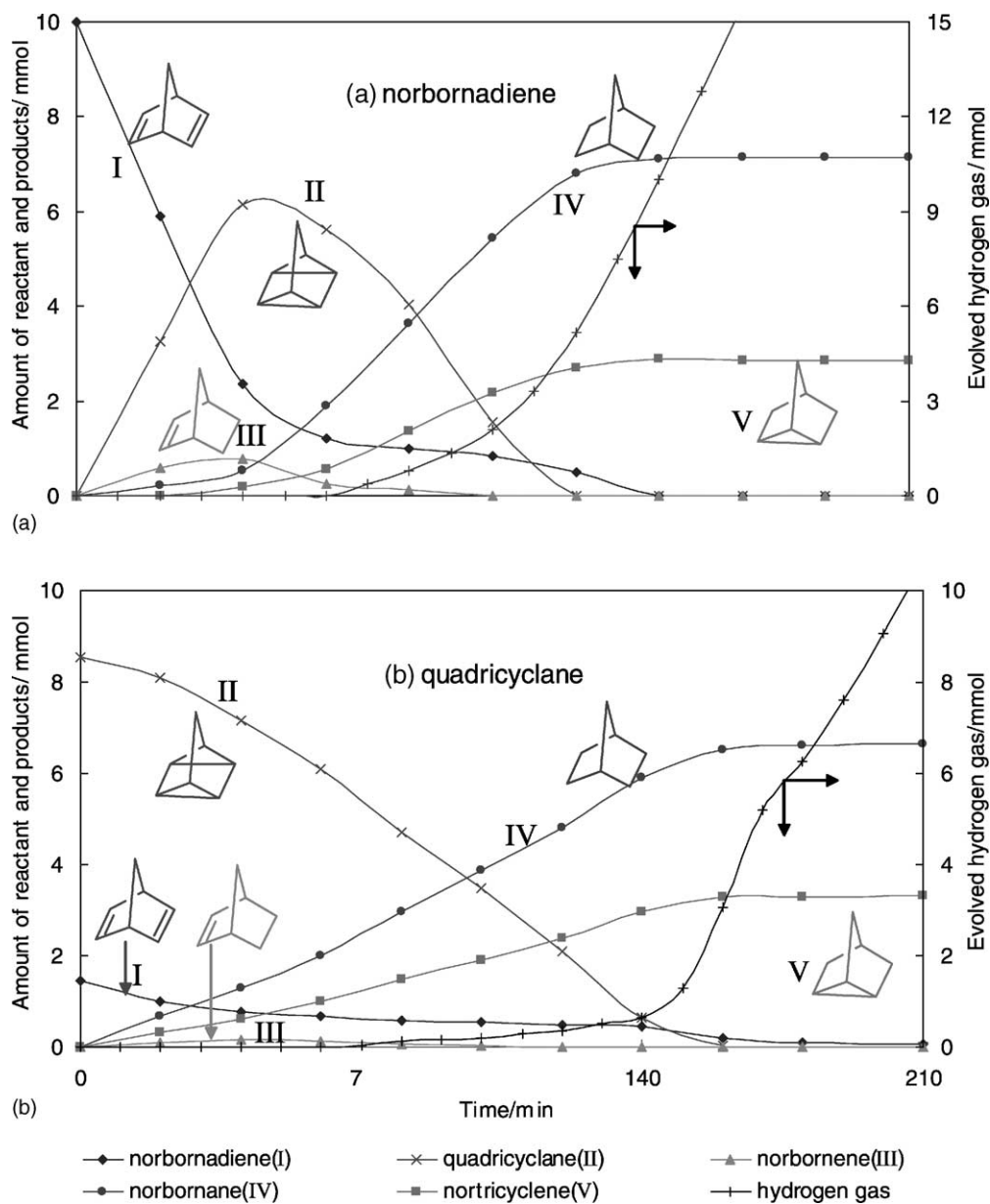
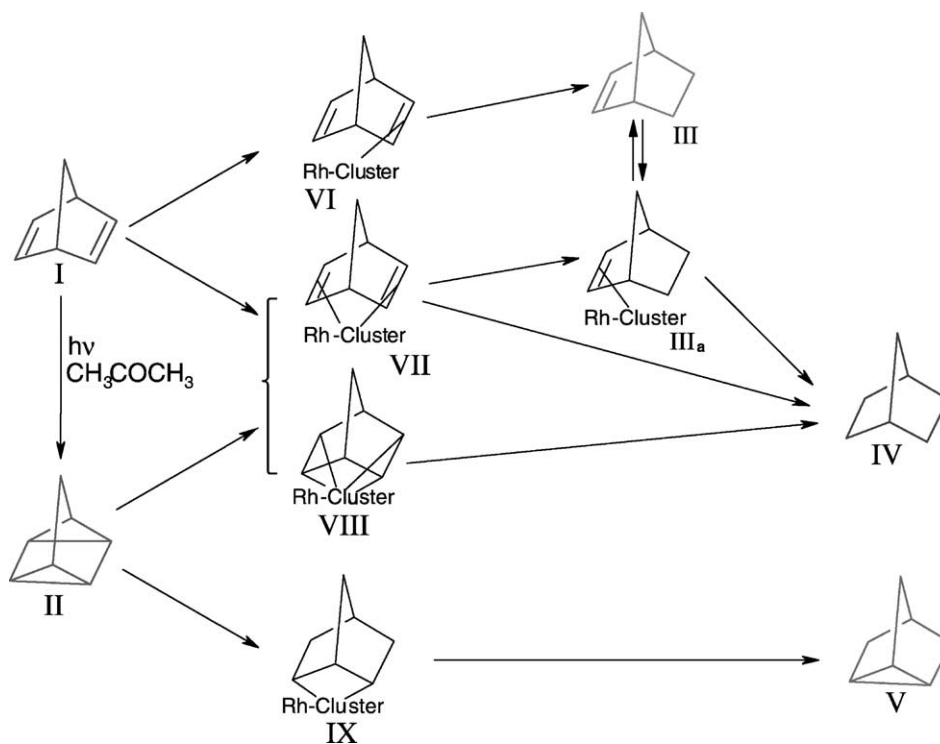


Fig. 1. Photo-assisted catalytic transfer hydrogenation of (a) norbornadiene and (b) quadricyclane. Reaction conditions: $\text{Rh}_6(\text{CO})_{16}$ as catalyst, 36 mg (0.033 mmol); acetone as photo-sensitizer, 3 cm^3 (40 mmol); 2-propanol as solvent, 170 cm^3 (2.8 mol); reactant, 1 cm^3 (9.8 mmol); reaction temperature, 15°C ; high pressure mercury lamp 100 W. (◆) Norbornadiene (I); (×) quadricyclane (II); (▲) norbornene (III); (●) norbornane (IV); (■) nortricyclene (V); (+) hydrogen gas.

It seems likely that the reaction paths are governed by acetone in the excited state. Actually, the excited acetone undergoes either triplet energy transfer to **I** to give **II** or hydrogen abstraction from 2-propanol to

give the 1-hydroxy-1-methylethyl radical. These two reactions are competitive, as shown in Scheme 2. Let us note that the rate for energy transfer leading to the valence isomerization (v_1) from **I** to **II** relative to the



Scheme 1. Mechanism for photo-assisted catalytic transfer hydrogenation and catalytic hydrogenation of norbornadiene and quadricyclane.

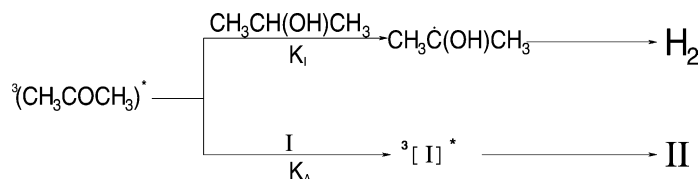
hydrogen abstraction rate (v_A) from 2-propanol may be expressed as

$$\frac{v_I}{v_A} = \frac{k_I[\text{excited acetone}][\text{I}]}{k_A[\text{excited acetone}][2\text{-PrOH}]} \quad (1)$$

where k_I and k_A indicate the rate constants of energy transfer and an electron transfer, respectively. Herein, the obtained ratio of v_I/v_A is about 36 at a rough estimate from Eq. (1) under our reaction conditions, if we make use of the rate constants for the reaction between excited acetone and 1,3-butadiene [10] instead of **I** and for ethyl alcohol [11] instead of 2-propanol.

We will be able to predict the reactivities with this kinetic consideration. Therefore, the valence isomerization (v_I) of **I** may be dominant over the hydrogenation (v_A) accompanied by the hydrogen abstraction due to kinetic reasons under our reaction conditions.

Then, can we observe the reaction directly from **I**? By the following kinetic analysis, we could find the reaction path directly from **I**. Thus, we can expect the occurrence of the direct hydrogenation of **I** at a lower concentration of **I**. In the reaction at 1/10 of the concentration of **I** (see Fig. 2), **III** was formed markedly and the formation **II** decreased. This shows



Scheme 2. Reactivities on roles of acetone in the photo-assisted catalytic transfer hydrogenation of **I** in 2-propanol.

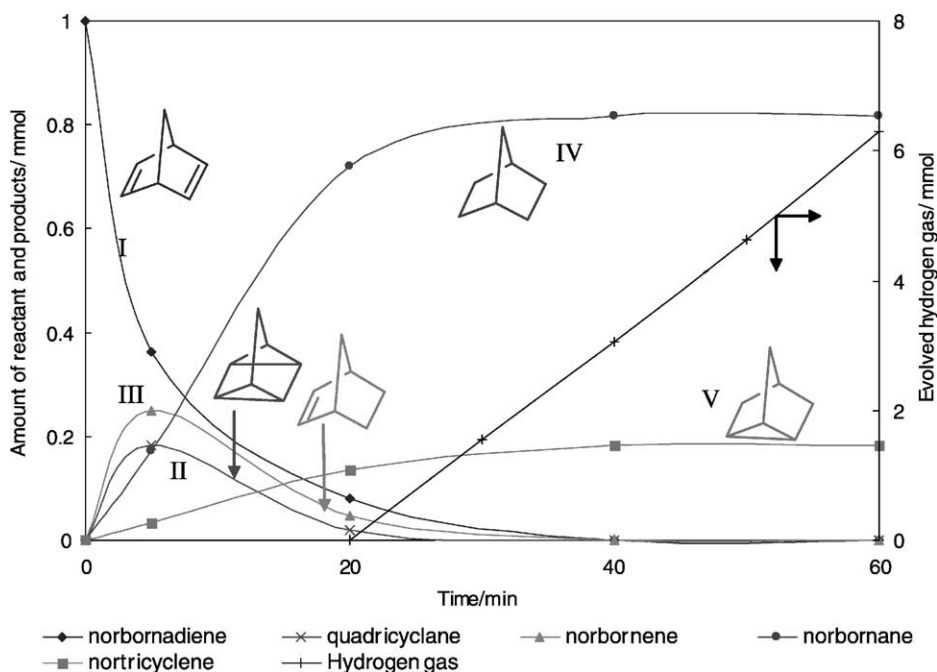


Fig. 2. Photo-assisted catalytic transfer hydrogenation at a lower concentration of norbornadiene. Reaction conditions: $\text{Rh}_6(\text{CO})_{16}$ as catalyst, 36 mg (0.033 mmol); acetone as photo-sensitizer, 3 cm^3 (40 mmol); 2-propanol as solvent, 170 cm^3 (2.8 mol); norbornadiene, 0.1 cm^3 (0.98 mmol); reaction temperature, 15°C high pressure mercury lamp 100 W. (◆) Norbornadiene; (×) quadricyclane; (▲) norbornene; (●) norbornane; (■) nortricyclene; (+) hydrogen gas.

that **I** is hydrogenated directly to **III** and **IV**. The most important point is the ratio of **IV/V** formation. In this case, the ratio of the **IV/V** formation is larger than that at a higher concentration of **I**, and the formation of **V** is correlated with the concentration of **II** formed during the reaction of **I**. Therefore, **V** is obviously formed from **II**.

The photo-assisted catalytic transfer hydrogenation of **III** is shown in Fig. 3. The compound **IV** was produced smoothly from **III** and no **V** was obtained from **III**, because **II** was never produced from **III**. Furthermore, the ratio of **IV/V** was almost the same in the reactions of **I** and **II**. From these results, the formation of **IV** mainly proceeded via the intermediates **IIIa** from **VII** or **VIII**, while **V** was produced preferentially from the intermediate **IX** via **II** in the photo-assisted catalytic transfer hydrogenation of **I** (see Scheme 1). The reaction mechanism on the photo-assisted catalytic transfer hydrogenation of **II** is able to be indicated by Scheme 1 as well as that of **I**.

3.2. Development of catalytic activity by pre-irradiation

As mentioned earlier, the activation of the rhodium cluster by pre-irradiation is necessary for the stable catalytic activity in the reaction of **I**. This can be explained by the kinetic consideration as mentioned above.

The activated Rh cluster catalyst species is considered to be produced by the removal of some carbonyl groups of $[\text{Rh}_6(\text{CO})_{16}]$ through the action of the 1-hydroxy-1-methylethyl radical, produced from 2-propanol and excited acetone. In this study, the potential energy of excitation for photo-isomerization of **I** to **II** seems to be lower than that for the photo-dehydrogenation of 2-propanol to 1-hydroxy-1-methylethyl radical. Therefore, the triplet energy transfer from excited acetone may proceed more rapidly to **I** than to 2-propanol. Consequently, the pre-photoactivation of $[\text{Rh}_6(\text{CO})_{16}]$ is necessary to produce real active catalyst species for

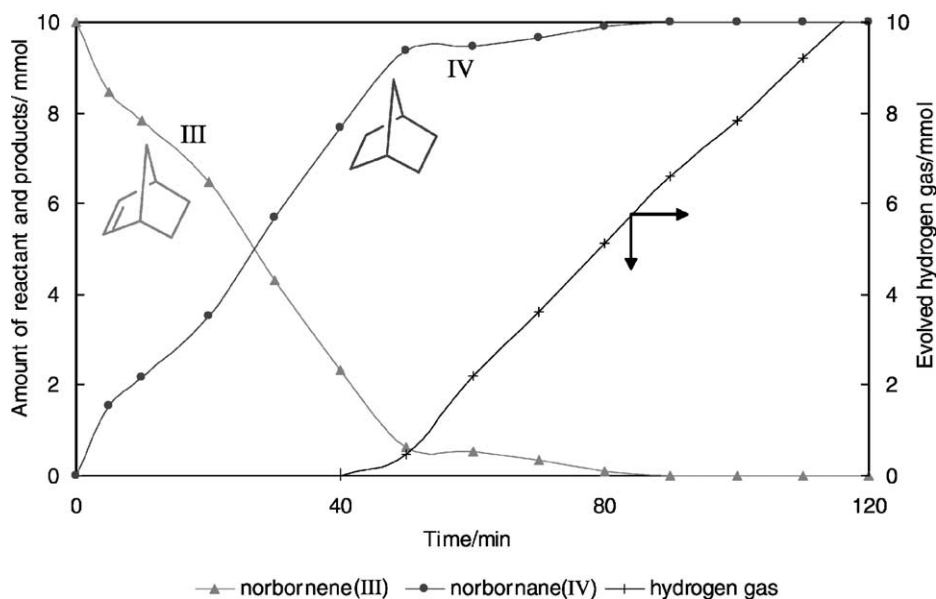


Fig. 3. Photo-assisted catalytic transfer hydrogenation of norbornene. Reaction conditions: $\text{Rh}_6(\text{CO})_{16}$ as catalyst, 36 mg (0.033 mmol); acetone as photo-sensitizer, 3 cm³ (40 mmol); 2-propanol as solvent, 170 cm³ (2.8 mol); norbornene, 925 mg (9.8 mmol); reaction temperature, 15 °C high pressure mercury lamp 100 W. (▲) Norbornene (III); (●) norbornane (IV); (+) hydrogen gas.

the photo-assisted catalytic transfer hydrogenation of **I**. Although the pre-photoactivation of $[\text{Rh}_6(\text{CO})_{16}]$ is not necessary for **II**, as for limonene [3], **II** was subjected to the reaction over the pre-activated catalyst in this study to obtain a better comparison with the reaction of **I**.

3.3. Catalytic hydrogenation without UV-light irradiation

It has been known that the catalytic hydrogenation of **I** over supported Pd catalysts proceeded stepwise [12]. The catalytic hydrogenation of **I** over the activated Rh cluster catalyst is shown in Fig. 4a. Compound **II** could not be observed in this reaction, which is distinct from the photo-assisted catalytic transfer hydrogenation of **I** under the activated Rh cluster catalyst. The yield (about 2%) of **V** was much smaller than that observed on the photo-assisted catalytic transfer hydrogenation of **I** with UV-light irradiation as reported by Fahey on Ru metal complex [9].

The stable intermediate **III** was obtained in a 38% maximum yield during the catalytic hydrogenation of **I**. The yield of **III** formed from **I** was larger than that

of the photo-assisted catalytic transfer hydrogenation. In addition, the ratio of **III/IV** formation was constant over a wide range up to about 60 min (see Fig. 4a). Probably, the catalytic hydrogenation of **I** proceeds in both successive and parallel fashions. In other words, it suggests that a part of **III** formed on the catalyst is rapidly hydrogenated to **IV** partly without desorption from the catalyst through the catalytic hydrogenation of **I** over the activated Rh cluster catalyst. The mode of the catalytic hydrogenation of **I** differs markedly from the photo-assisted catalytic transfer hydrogenation.

The catalytic hydrogenation of **II** (96% pure) over the activated Rh cluster catalyst is shown in Fig. 4b. In this reaction, the valence isomerization from **II** to **I** seems not to occur because **I** does not further increase during these reactions (see Figs. 1b and 4b). Generally, it exhibited features similar to the photo-assisted catalytic transfer hydrogenation of **II**. Compound **IV** is obtained from **II** and **V** is formed via intermediate **IX** as in the case of the photo-assisted catalytic transfer hydrogenation. The ratio of the **IV/V** formation was 6 for the catalytic hydrogenation while it was 3 for the photo-assisted catalytic transfer hydrogenation. The catalytic hydrogenation of **II** over the

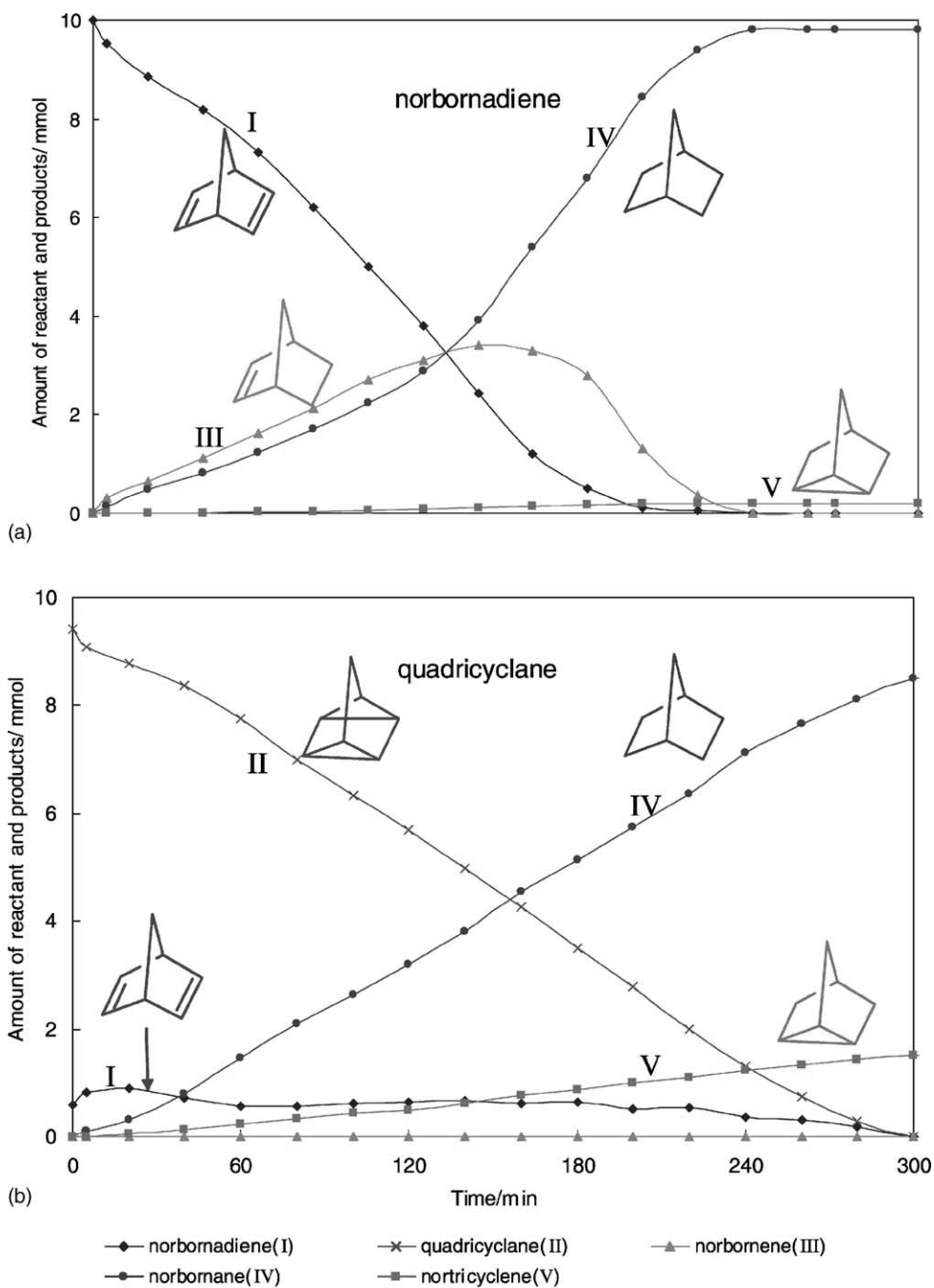


Fig. 4. Catalytic hydrogenation of (a) norbornadiene and (b) quadricyclane. Reaction conditions: $\text{Rh}_6(\text{CO})_{16}$ as catalyst, 36 mg (0.033 mmol); 2-propanol as solvent, 170 cm^3 (2.8 mol); reactant, 1 cm^3 (9.8 mmol); reaction temperature, 30°C . (◆) Norbornadiene (I); (×) quadricyclane (II); (▲) norbornene (III); (●) norbornane (IV); (■) nortricyclene (V).

activated Rh cluster catalyst gave mainly **IV** rather than **V**. Therefore, the formation of **V** from **II** seems to be achieved under UV-light irradiation.

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