Photo-Assisted Hydrogen Transfer from Alcohol to Limonene Catalyzed by $[Rh_6(CO)_{16}]$

Akihisa Yanagawa, Tomomi Hatae, Satoru Yada, Akira Sugimori, and Yuzuru Takagi*
College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajousui, Setagaya-ku, Tokyo 156-8550

(Received May 18, 1999; CL-990399)

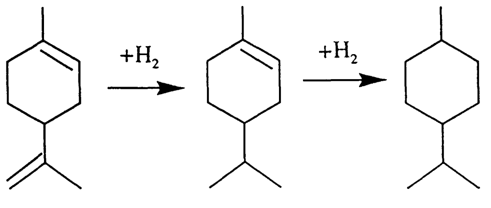
Partial hydrogenation of the *exo*-olefinic bond in limonene to carvomenthene proceeds smoothly by photocatalytic hydrogen transfer from 2-propanol using $[Rh_6(CO)_{16}]$ as a catalyst under UV-irradiation in the presence of acetone. Hydrogen gas evolves after the formation of carvomenthene has been completed. 1-Hydroxy-1-methylethyl radical formed in the reaction of photochemically excited acetone with 2-propanol serves both as an activator for the catalyst and as a hydrogen source.

Photo-assisted dehydrogenation of alcohols and the evolution of hydrogen has been known to occur over metal complex catalysts.[1] However, the hydrogenation of olefins has scarcely been studied over metal carbonyl cluster catalysts,[2] though it occurs over a wide range of transition metal complexes and/or photo-generated catalysts under UV-light.[3] Furthermore, the studies on the coupled photoreaction systems for the dehydrogenation of alcohols and the hydrogenation of organic compounds by hydrogen transfer have not been so much investigated over Rh carbonyl cluster catalysts under UV light irradiation.

In this paper, we describe the selective photo-assisted hydrogenation of limonene (**1**) by hydrogen transfer from 2-propanol over tetra-μ^3-carbonyldodecacarbonylhexarhodium $[Rh_6(CO)_{16}]$.[4] In addition, the reaction mechanism and catalytically active species are briefly considered.

The reaction was carried out with **1** (1 cm^3, 6.2 mmol), acetone (3 cm^3, 40 mmol), and 2-propanol (150 cm^3) under argon gas in a pyrex glass vessel (200 cm^3). The Rh carbonyl cluster (36 mg) was dispersed in the reaction mixture and stirred magnetically, and then the reaction was initiated by the irradiation with a 100 W high pressure mercury lamp at 25 ℃. The reaction mixture was analyzed by gas-chromatography.

Usually, the catalytic hydrogenation of limonene is a consecutive reaction as Scheme 1.



Limonene (**1**) Carvomenthene (**2**) *p*-Menthane(**3**)

Scheme 1. Catalytic hydrogenation of limonene.

The time course of the photoreaction is represented in Figure 1. After several minutes of an induction period, carvomenthene (**2**) is formed. The yield of **2** reaches a maximum (yield, 60%) at 50 min of irradiation under our conditions. At this point, hydrogen gas comes to evolve and the hydrogenation of **2** to *p*-menthane (**3**) proceeds slowly. A small amount of 3-*p*-menthene formed by the isomerization of **2** is observed as a by-product.

The important role of acetone in the photo-assisted dehydrogenation of 2-propanol has been found by Grätzel et al.[5] For our photocatalytic hydrogen transfer reaction, the presence of acetone is indispensable. In the absence of acetone **2** was not obtained, although hydrogen gas was evolved in the UV light irradiation of the 1-2-propanol-$[Rh_6(CO)_{16}]$ system.

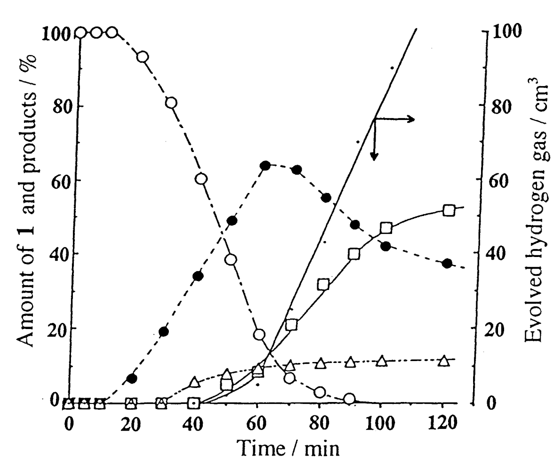
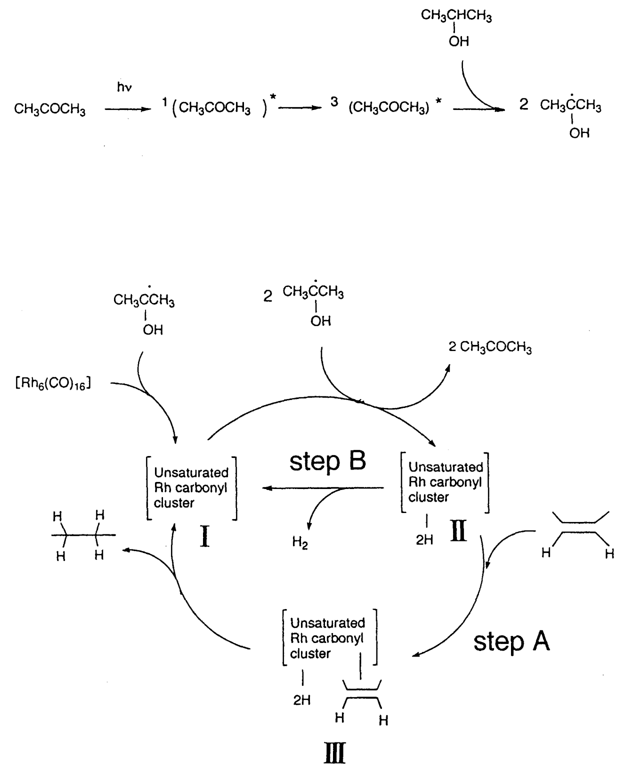


Figure 1. Photo-assisted hydrogen transfer from 2-propanol to limonene catalyzed by $[Rh_6(CO)_{16}]$ catalyst. ○: Limonene, ●: Carvomenthene, □: *p*-Menthane (*cis* +*trans*), △: 3-*p*-Menthene, · : H_2 evolved.

From the results described above, we assume that 1-hydroxy-1-methylethyl radical is first formed from 2-propanol by the excited acetone under UV light irradiation,[6] and then 1-hydroxy-1-methylethyl radical would likely pull out the carbon monoxide from the $Rh_6(CO)_{16}$ catalyst, thus the coordinatively unsaturated active species (unsaturated Rh carbonyl cluster I) is formed, consequently. Actually, the infrared spectrum of the complex recovered from the solution of the reaction mixture after this photo-assisted reaction was similar to that of the $[Rh_6(CO)_{14}]^{4-}$ complex with respect to CO stretching vibration.[7]

For this photoreaction system, we propose scheme 2 as a possible reaction mechanism of the photo-assisted hydrogenation of limonene (**1**) over the coordinatively unsaturated Rh carbonyl cluster under UV light irradiation. The active species labeled II is formed by the transfer of a hydrogen from 1-hydroxy-1-methylethyl radicals to the unsaturated Rh carbonyl cluster I (See Scheme 2). The transfer of two hydrogen atoms to **1** gives **2** *via* the step A of the cycle in the first stage of the reaction.

As can be seen from Figure 1, the hydrogenation of **2** begins after **1** has been completely consumed. It suggests the difference in the affinity of **1** and **2** to the unsaturated Rh carbonyl cluster II.



Scheme 2. Proposed mechanism for photo-assisted hydrogen transfer from 2-propanol to limonene catalyzed by $Rh_6(CO)_{16}$.

Acetone formed successively by the photo-assisted dehydrogenation of 2-propanol seems to depress strongly the photo-assisted hydrogenation of **2** in this reaction (See Figure 1). In fact, the addition of 1 cm^3 of acetone in 40 min after the start of the reaction completely inhibited the hydrogenation of **2** to **3** (See Figure 2).[8] The affinity of **2** to the unsaturated Rh carbonyl cluster I should be weaker than that of acetone.

In progress of our reaction, the increase of the concentration of acetone depresses the hydrogenation of **2**. In the second stage of the reaction, the formation of acetone and the evolution of the hydrogen occurs in the step B of the cycle.

The hydrogenation of **1** rarely takes place under a hydrogen pressure of 0.1 MPa with $Rh_6(CO)_{16}$ complex catalyst in the presence of acetone without UV light irradiation. It should be noteworthy that the coordinatively unsaturated rhodium cluster formed in the UV light irradiation in 2-propanol in the presence of acetone has catalytic activity for hydrogenation of **1** using H_2 in the dark.

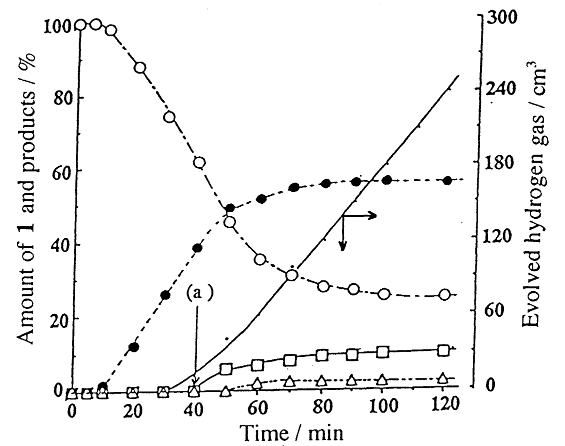


Figure 2. Effect of added acetone on the photo-assisted hydrogen transfer from 2-propanol to limonene catalyzed by $[Rh_6(CO)_{16}]$ catalyst. ○: Limonene, ●: Carvomenthene, □: *p*-Menthane(*cis* +*trans*), △: 3-*p*-Menthene, • : H_2 evolved. (a) Further addition of acetone (1 cm^3).

References and Notes

1 a) H. Arakawa and Y. Sugi, *Chem. Lett.*, **1981**,1323. b) H. Moriyama, T. Aoki, S. Shinoda, and Y. Saito, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 369.

2 M. S. Wrighton, J. L. Graff, C. L. Reichel, and R. D. Sanner Report **1979**, TR16; *Chem, Abstr.*, **91**, 199513 (1979).

3 G.L.Geoffroy and M.S.Wrighton, in " Organometallic Photochemistry, " Academic Press, New York (1979).

4 P.Chini, *Chem. Commun.*, **1967**, 440.

5 C. K. Grätzel and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7741 (1979).

6 In this photoreaction, we detected 2,3-dimethyl-2,3-butanediol, a coupling product from 1-hydroxy-1-methylethyl radicals, by means of GC-MS as reported by Saito and co-workers. See, a) H. Yamamoto, S. Shinoda, and Y. Saito, *J. Mol. Catal.*, **30**, 259 (1985); b) T. Takahashi, S. Shinoda, and Y. Saito, *ibid.*, **31**, 301 (1985).

7 P. Chini, G. Longori, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).

8 This hydrogen transfer reaction has been found practically not to proceed, when acetone was added either in much greater or much smaller amounts than 3 cm^3.