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Thermal Dehydrogenation of Cyclooctane by Supported Noble Metal Catalysts

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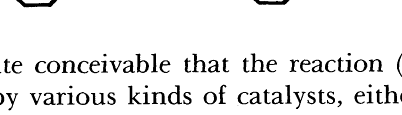
Under boiling and refluxing conditions, cyclooctane has been dehydrogenated to cyclooctene and molecular hydrogen selectively with carbon- and alumina-supported Pd, Ph, and Ru catalysts. The activity order among these metal catalysts was Pd>Rh>Ru. The most active carbon-supported Pd catalyst was least sensitive to the rate retardation caused by cyclooctene adsorption. Desorption of molecular hydrogen from the Pd catalyst surface was deduced to proceed rapidly after the rate-determining step.

The reaction of alkane dehydrogenation yielding alkene and molecular hydrogen (Eq. 1) is highly endothermic.[1)]

$$\text{alkane} \longrightarrow \text{alkene} + H_2. \qquad (1)$$

High temperatures were required for this reaction in general,[2)] as exemplified by styrene formation from ethylbenzene,[3)] and with the various processes for petroleum reforming[4)] due to the high endothermicity and the increase in the number of molecules. On the contrary, homogeneous transition metal catalysts dehydrogenated alkanes under mild temperatures, where photoirradiation was considered to be indispensable.[5)]

It is possible, however, to get rid of the equilibrium restriction imposed at mild temperatures, as long as the product hydrogen is somehow removed from the reaction medium. The boiling and refluxing conditions fulfill the present requirement for the reaction. (Eq. 1) Under boiling conditions, the vapor phase in contact with the catalyst solution is full of the solvent components, whereas the refluxing procedure separates molecular hydrogen from the vapor phase. Since hydrogen is eliminated from the solution after its catalytic generation and is not allowed to dissolve into the solution, alkane dehydogenation can proceed catalytically at mild temperatures without photoirradiation, if we have any suitable catalyst. Recently, in fact, we observed the catalytic dehydrogenation of cyclooctane at 151 °C, yielding cyclooctene and molecular hydrogen (Eq. 2) using Wilkinson complex $RhCl(PR_3)_3$.[6)]



(2)

It is quite conceivable that the reaction (Eq. 2) is catalyzed by various kinds of catalysts, either homogeneous or heterogeneous. The metallic hydrogenation catalyst is a good candidate, since the metallic surface sites of hydrogenation catalysts are capable of dissociating the C–H bonds of alkane and to form molecular hydrogen from surface hydrogen species.

In the present study we attempted to find supported metal catalysts for cyclooctane dehydrogenation under boiling and refluxing conditions.

Experimental

After the treating with a mixture of concd H_2SO_4 and HNO_3 in order to remove unsaturated hydrocarbon impurities, cyclooctane was dried over $CaCl_2$ and distilled under a nitrogen atmosphere in the presence of metallic sodium. The 5 wt% supported noble metal catalysts (metals: Pd, Rh, and Ru; supports: carbon and alumina) were provided from N. E. Chemcat Co. Carbon-supported catalysts were preliminarily dried by heating in N_2 stream for about 1 h and under vacuum for about 30 min at 180 °C. All of the catalysts were pretreated with H_2 (1 atm, 180 °C, 30 min), followed by evacuation (180 °C, 10 min) before use.

All manipulations were carried out under a nitrogen atmosphere. The catalysts (0.2 mmol-metal) were suspended in cyclooctane (100 ml) in a Schlenk tube (200 ml). The suspension was heated with an oil bath (180 °C) and kept boiling at 151 °C. After the suspension began to boil, the amount of evolved gas was measured by a gas buret (50 ml) through a reflux condenser; the gas composition was analyzed by gas chromatography using an active carbon column. After the reaction, the solution from which the catalyst was removed by sedimentation was analyzed by GC (OV-1 and PEG-20M capillary columns).

Results and Discussion

Dehydrogenation of Cyclooctane under Boiling and Refluxing Conditions. The time courses of gas evolution are shown in Fig. 1. Hydrogen was yielded exclusively with the Pd/C catalyst, whereas the Ru/Al_2O_3 catalyst gave methane as a by-product at a 10% level. Gaseous products from the other four catalysts were mainly hydrogen and methane (under 0.2%). On the other hand, only cyclooctene was detected as the dehydrogenation product in the liquid phase. The amounts of hydrogen and cyclooctene produced after a 24 h reaction are show in Table 1. The stoichiometric coincidence was satisfactory. Since the turnover number (per metal-mol) was apparently over 1, the reaction of alkane dehydrogenation (Eq. 1) was demonstrated to proceed catalytically, even under

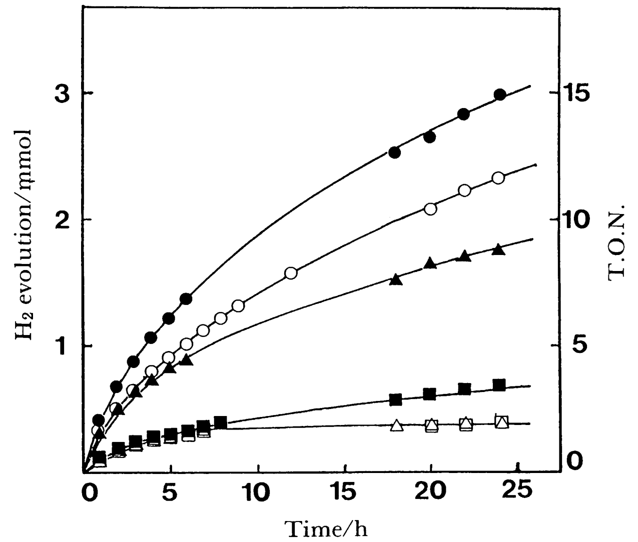


Fig. 1. Time-course plots of H_2 evolution from cyclooctane suspended with Pd (5%)/C (●), Pd (5%)/Al_2O_3 (○), Rh (5%)/C (▲), Rh (5%)/Al_2O_3 (△), Ru (5%)/C (■), and Ru (5%)/Al_2O_3 (□) at the concentration of 0.2 mmol metal/100 ml under boiling and refluxing conditions (151 °C).

Table 1. Dehydrogenation Products of Cyclooctane with Suspended Noble Metal Catalyst under Boiling and Refluxing Conditions

Catalyst	H_2/mmol	Cyclooctene/mmol
Pd (5%)/C	2.97	2.88
Pd (5%)/Al_2O_3	2.30	2.20
Rh (5%)/C	1.74	1.57
Rh (5%)/Al_2O_3	0.37	0.36
Ru (5%)/C	0.59	0.52
Ru (5%)/Al_2O_3	0.36	0.34

Catalyst concentration: 0.2 mmol metal/100 ml; Reaction temperature: 151 °C; Reaction time: 24 h.

mild conditions at 151 °C.

The activity order was Pd>Rh>Ru,[7] where the carbon-supported catalysts were more active than the alumina-supported ones. This activity order among metals was completely different from that of 2-propanol dehydrogenation (Ru>Rh>Pt>Pd),[8] and rather similar to that of cyclohexanol dehydrogenation (Pd>Rh>Pt>Ru).[9] Since the reaction temperatures (boiling point) of cyclooctane (151 °C) and cyclohexanol (161 °C) are comparable, whereas that of 2-propanol (82.4 °C) is considerably low, the low reaction rate for the Pd catalysts to evolve hydrogen from 2-propanol may be ascribed to the high stability of hydrogen in the metal hydride phase at low-temperature regions.[10]

Retardation Effects of Added Cyclooctene. The retardation effects of product cyclooctene on the reaction rates were examined about Pd/C, Pd/Al_2O_3, and Rh/C catalysts, which exhibited relatively high activities. Figure 2 shows the time courses of hydrogen evolution from the suspensions containing cyclooctene at various concentrations with these catalysts. Little retardation was found for the most active Pd/C catalyst, while the Pd/Al_2O_3 and Rh/C catalysts were considerably inhibited by added cyclooctene.

The relationship between the initial rates of hydrogen evolution (v) and the concentrations of added cyclooctene ([COE]) was analyzed with Eq. 3 while taking account of retardation due to cyclooctene adsorption.

$$v = k/(1 + K[\mathrm{COE}]). \qquad (3)$$

As shown in Fig. 3, plots of $1/v$ and [COE] gave straight lines; the values of k and K are summarized in Table 2. The order of the rate constant (k) was Pd/C>Pd/Al_2O_3>Rh/C, whereas the retardation con-

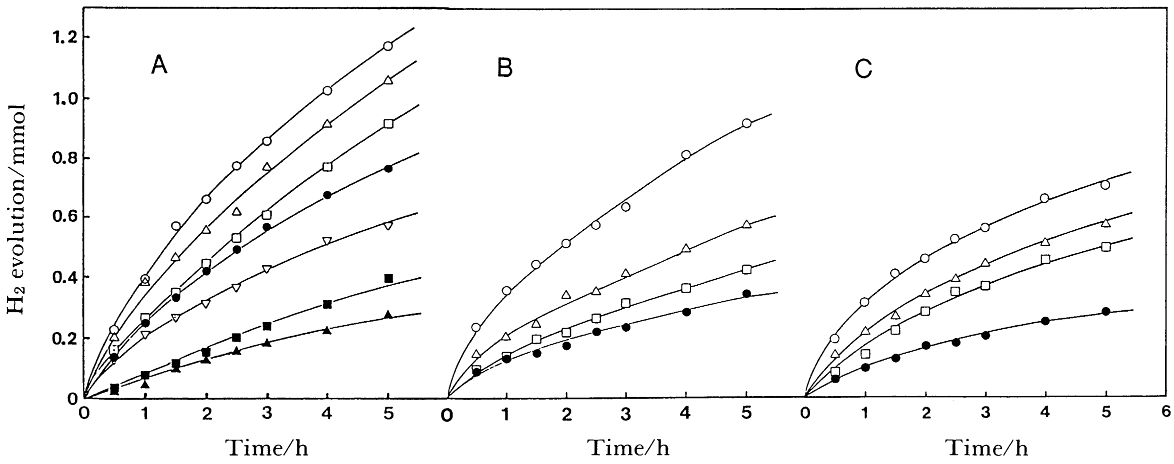


Fig. 2. Effect of cyclooctene addition on H_2 evolution from cyclooctane suspended with noble metal catalysts (0.2 mmol metal/100 ml) under boiling and refluxing conditions (151 °C). Catalyst: (A) Pd/C, (B) Pd/Al_2O_3, and (C) Rh/C. Addition of cyclooctene: 0 μl (○), 25 μl (△), 50 μl (□), 100 μl (●), 150 μl (▽), 300 μl (■), and 450 μl (▲).

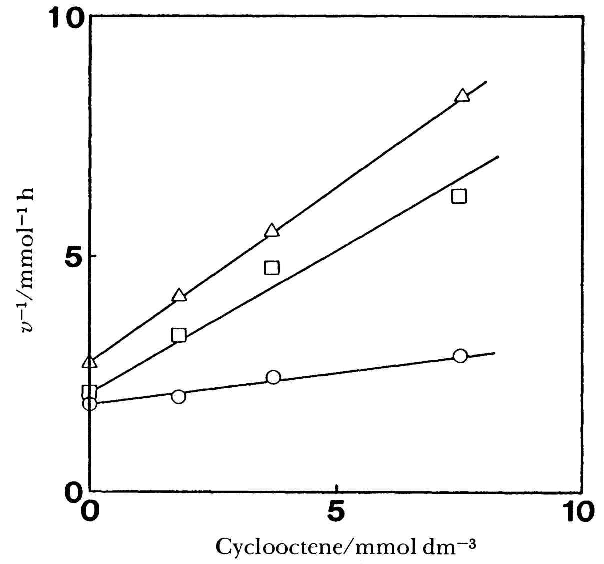


Fig. 3. Rate retardation due to cyclooctane analyzed with equation 3 for Fig. 2. Catalyst: Pd/C (○), Pd/Al_2O_3 (□), and Rh/C (△).

Table 2. Rate Constant (*k*) of Cyclooctane Dehydrogenation and Retardation Constant due to Cyclooctene Absorption (*K*) Calculated from Fig. 3

Catalyst	*k*/mmol h^{-1} g^{-1}	*K*/mmol^{-1} dm^3
Pd/C	26	0.075
Pd/Al_2O_3	22	0.270
Rh/C	17	0.250

stant (*K*) of the Pd/C catalyst was extremely smaller than those of the other catalysts, indicating the facile desorption of alkene from the Pd/C catalyst surface.

Rate Retardation Caused by 1-Nonene Addition. 1-Nonene (0.58 mmol, corresponding to the amount of added cyclooctene in the former section) was added to cyclooctane suspended with the Pd/Al_2O_3 catalyst, since this catalyst exhibited a relatively high activity for cyclooctane dehydrogenation and rate retardation due to added cyclooctene. Hydrogen evolved from a solution containing 0.58 mmol of 1-nonene and from one containing 0.78 mmol of cyclooctene; after reaction for 3 h it amounted to 0.20 mmol and 0.24 mmol, respectively, indicating that the rate retardations caused by these alkenes are comparable to each other.

Figure 4 shows the amounts of hydrogen evolved and the reaction products in solution, allowing a comparison of the effect of added 1-nonene with that of no alkene added.

Both hydrogen evolution (0.20 mmol) and intermolecular hydrogen transfer from cyclooctane to 1-nonene (0.30 mmol) proceeded simultaneously, while 1-nonene was isomerized exclusively to *cis*-2-nonene (0.11 mmol). It is noteworthy that the intermolecular hydrogen transfer proceeds more rapidly than does isomerization. The total amounts of nonane and hydrogen (0.5 mmol) were nearly equal to that of cyclooctene (0.60 mmol) produced. The coincidence of these magnitudes with that of hydrogen evolved from alkene-free cyclooctane (0.64 mmol) indicates that both hydrogen evolution and transfer proceed at common active sites.

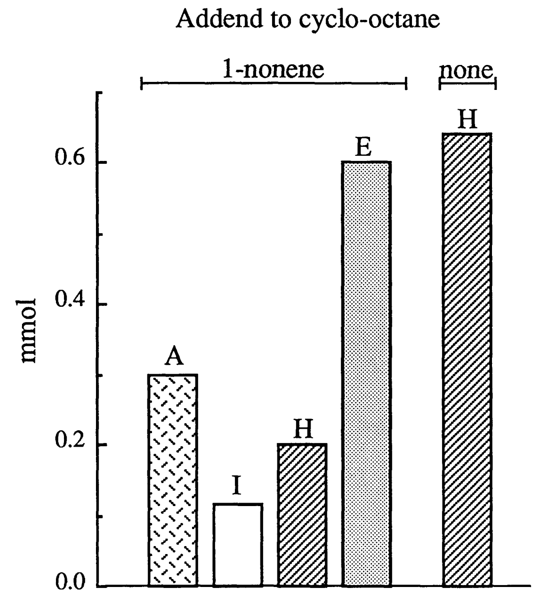


Fig. 4. Effect of alkene addition to hydrogen evolution or transfer from cyclooctane with suspended Pd catalyst under boiling and refluxing conditions. H: hydrogen, A: nonane, E: cyclooctene, I: isomerized nonene (exclusively *cis*-2-nonene). Catalyst: Palladium (5%)/alumina 0.2 mmol. Substrate: Cyclooctane (100 ml). Added alkene: 1-nonene (0.58 mmol). Reaction temperature: 151 °C, Reaction time: 3 h.

Reaction Mechanism of Dehydrogenation. The mechanism of alkane dehydrogenation on heterogeneous catalysts, yielding alkene and molecular hydrogen via adsorbed species on the active site (ads), has been proposed at high temperature regions:[11]

$$\text{alkane} \longrightarrow \text{alkane(ads)}, \tag{4}$$

$$\text{alkane(ads)} \longrightarrow \text{alkyl(ads)} + \text{H(ads)}, \tag{5}$$

$$\text{alkyl(ads)} \longrightarrow \text{alkene(ads)} + \text{H(ads)}, \tag{6}$$

$$\text{alkene(ads)} \longrightarrow \text{alkene}, \tag{7}$$

and

$$2\text{H(ads)} \longrightarrow H_2. \tag{8}$$

As for dehydrogenation using homogeneous catalysts, the reaction schemes on the reductive elimination of ligand hydrides under photoirradiation, as well as thermal hydrogen transfer from alkane to alkene and the photocatalytic cycle of hydrogen evolution from alkane, have been discussed.[12] In view of endothermicity, the evolution of molecular hydrogen from the hydride intermediate species is more difficult than hydrogen transfer to alkane.

Nonane formation from 1-nonene by the intermolecular hydrogen transfer strongly suggests the possibility for a hydrogen species on the catalyst surface to react with not only 1-nonene, but also cyclooctene, which remains on the dehydrogenation site or is adsorbed from the solution bulk. Cyclooctane should be regenerated from the surface hydrogen species and cyclooctene by hydrogen-transfer, since nonane was formed from 1-nonene.

$$\text{alkene} \longrightarrow \text{alkene(ads)}, \qquad (9)$$

$$\text{alkene(ads)} + 2\text{H(ads)} \longrightarrow \text{alkane}. \qquad (10)$$

It is therefore reasonable to assume that the rate retardation for hydrogen evolution caused by alkenes is brought about from a consumption of adsorbed hydrogen species by forming alkane, in addition to the site-occupation effect, owing to alkene adsorption. Since they are commonly governed by the amounts of adsorbed alkene, these retardation effects are expressed by the same rate equation (Eq. 3). In view of the standard Gibbs energy changes, the hydrogen transfer from cyclooctane to 1-nonene or from cyclooctane to cyclooctene (Eq. 11) proceeds more rapidly than does hydrogen evolution (Eq. 2) in this reaction temperature region.

$$\text{alkane} + \text{alkene}' \longrightarrow \text{alkene} + \text{alkane}'. \qquad (11)$$

Provided that the hydrogen evolution step (Eq. 8) is rate-determining in the hydrogen evolution reaction, the adsorbed hydrogen species would be abundant on the catalyst surface, being sufficiently supplied from cyclooctane. The exothermic and facile nonane formation from 1-nonene would surpass the endothermic molecular hydrogen formation from the surface hydrogen species. However nearly equal rates were observed for nonane formation and hydrogen evolution in the absence of alkene, indicating that the step of molecular hydrogen formation is preceded by the rate-determining step. With regard to the reaction of molecular hydrogen formation from cyclooctane using the suspended Pd/Al_2O_3 catalyst, it is therefore plausible that either C–H bond cleavage of cyclooctane or β-hydrogen elimination of the adsorbed cyclooctyl species is rate-determining.

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