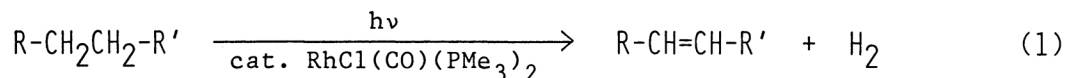


Highly Catalytic Dehydrogenation of Alkanes to Olefins via C-H
Activation in the Presence of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under Irradiation

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Olefins and dihydrogen were catalytically formed from alkanes
at an ambient temperature in the presence of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under
irradiation.

It is a great challenge to directly functionalize hydrocarbons (especially alkanes) under mild conditions with metal complexes. We recently reported the several examples via catalytic C-H activation such as carbonylation,¹⁻⁴⁾ dehydrogenative dimerization,⁵⁾ isocyanide insertion,⁶⁾ and silylation⁷⁾ in the presence of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under irradiation. Another interesting subject is dehydrogenation of alkanes to yield olefins. Although some investigation on this subject has been reported by Crabtree and Felkin,⁸⁾ most of the papers have used t-butylethylene as a hydrogen acceptor. Crabtree also reported that cyclooctene could be formed even without the hydrogen acceptor under photo-assisted conditions using an iridium hydride as the catalyst.⁹⁾ The catalytic activity was, however, very low (7 turnovers after 7 days). A dehydrogenation of pentane with an iron complex has recently been proposed by Field et al.¹⁰⁾ But the catalytic reaction has not been achieved owing to the secondary reaction of the product (1-pentene). We now wish to report the application of the $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ system to dehydrogenation of alkanes resulting in remarkably high catalytic activity (Eq. 1).



A typical reaction procedure was as follows. A 0.7 mM solution of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ in cyclohexane (30 cm³) was irradiated by a 100 W high pressure mercury lamp (UVL-100HA, Riko Corp.) at an ambient temperature for 16.5 h. The irradiation was conducted under nitrogen atmosphere in a closed system. The GC analysis of the reaction mixture revealed the formation of cyclohexene (138 turnovers) and benzene (3 turnovers). A nearly theoretical amount of dihydrogen (132 turnovers) was detected in the gas phase. Non-cyclic alkane (hexane) could be also dehydrogenated to yield hexenes (155 turnovers after 27 h). The 2-hexene (cis/trans = 1/3) was the major regioisomer (the regioisomeric ratio of 1-, 2-, and 3-hexenes was 1 : 79 : 20). The isomerization of the double bond, however, seemed to occur during the dehydrogenation reaction,¹¹⁾ because the 1-

hexene/2-hexene ratio gradually decreased.

In order to prevent the influence of the reverse reaction (hydrogenation), the dehydrogenation of cyclohexane was carried out under a slow stream of nitrogen (8 ml/min). The reaction was accelerated (195 turnovers after 16.5 h) compared with that in the closed system. Cyclooctane was also dehydrogenated under a nitrogen flow. The reaction mixture appeared homogeneous even after 100 h. The initial turnover frequency was 40 h^{-1} and the turnover number reached 930 after 68.5 h (8% conversion of cyclooctane). The dehydrogenation mechanism is presumably attributable to the β -hydrogen elimination of the alkyl(hydrido)rhodium species formed through the oxidative addition of the alkane C-H bond to the photogenerated $\text{RhCl}(\text{PMe}_3)_2$.³⁾

In summary, this paper offers the first example of practically productive dehydrogenation of alkanes via the transition metal complex-catalyzed C-H activation. The present system is especially promising in the following two points; no need of hydrogen acceptor and the quite high catalytic activity. The improvement of the catalytic activity by controlling the reaction conditions and the extension to various substrates are now under investigation.

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