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Inert Solvent for Catalytic C-H Activation.
Achievement of High Conversion in Dehydrogenation of Alkane

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High conversions are achieved in photo-assisted dehydrogenation of alkane catalyzed by $RhCl(CO)(PMe_3)_2$ using bulky hydrocarbons like 2,2,5,5-tetramethylhexane and 1,3,5-tri-*t*-butylbenzene as inert solvents. Main by-product in cyclooctane dehydrogenation at a high conversion is 1,3-cyclooctadiene.

Recently we have developed an effective dehydrogenation of alkane catalyzed by Vaska type rhodium complexes under irradiation (Eq. 1).1) One principal problem in these reactions is that a substrate itself must be used as a solvent, because usual solvents having C-H bonds are also reactive under the reaction conditions. This has strongly restricted the achievement of high conversions and application of the procedure to substrates which are expensive and/or of high melting points. Bergman has proposed the use of liquid xenon as an inert solvent for the stoichiometric C-H activation by $Cp^*Ir(PMe_3)$.2) However, liquid xenon is not practical to use for our catalytic system because of its very low boiling point. Hence, development of an inert solvent for the $RhCl(CO)(PMe_3)_2$-hν system is strongly desired.

$$\text{R-CH}_2\text{-CH}_2\text{-R'} \xrightarrow{h\nu,\ \text{RhCl(CO)(PMe}_3)_2} \text{R-CH=CH-R'} + \text{H}_2 \qquad (1)$$

Since Graham reported the activation of methane C-H bond by $Cp^*Ir(CO)_2$ under irradiation in a perfluoroalkane as an inert solvent,3) we first attempted to use some perfluoroalkanes as a solvent. However, most of them were completely immiscible with hydrocarbon substrates. Moreover, the Vaska type rhodium complex was not soluble in perfluoroalkanes, either. Although perfluorobenzene showed a good solubility for both hydrocarbons and the rhodium catalyst, it reacted with olefins formed under irradiation.[4)] Next, we investigated the use of bulky hydrocarbons which were expected to remain intact during the dehydrogenation process because of steric bulkiness (Table 1). Thus, we have found that 2,2,5,5-tetramethylhexane (**1**) and 1,3,5-tri-*t*-butylbenzene (**2**) are inert solvents for the dehydrogenation catalyzed by the $RhCl(CO)(PMe_3)_2$-hv system. The former is easily prepared by the Wurtz coupling of neopentyl iodide synthesized from neopentyl alcohol.[5)] The latter is commercially available.

When **1** was used as the solvent, more than 90% of cyclooctane (initial concentration 2 vol.%) was dehydrogenated to give mainly cyclooctene (COE) and 1,3-cyclooctadiene (1,3-COD) (Run 1). The amount of dimers (mainly cyclooctenylcyclooctene)[1a)] was much less than that of COD. This means that β-hydride elimination from cyclooctyl (or cyclooctenyl) rhodium intermediates leading to dehydrogenation is much faster than C=C double bond insertion to these complexes. Worth noting here is that dilution of cyclooctane with **1** did not reduce the initial turnover rate so much as compared with the reaction of neat cyclooctane (Run 2). This strongly suggests that oxidative addition of a C-H bond to the rhodium complex is not the rate determining step in the present dehydrogenation.[1a)] COD and dimers seem to be secondary products formed from COE. In fact, the dehydrogenation of COE under similar conditions led to the formation of 1,3-COD and dimers (21 and 5% yields after 1 h, respectively). Regioselective formation of 1,3-COD is presumably ascribed to the preferential activation of an allylic C-H bond of COE. This is in good agreement with the fact that a C_2-branched diene was formed in the dehydrogenative dimerization of 1-decene by the present catalytic system.[6)] The possible dehydrogenation product of the solvent, 1,2-di-*t*-butylethylene was not detected at all. When the catalyst concentration was reduced from 2 mM to 0.5 mM, a higher turnover number was easily achieved (Run 3). A very bulky aromatic hydrocarbon **2** also allowed high conversions although the reaction in **2** was a little slower than in **1** (Run 4). Neohexane, when used as a solvent, was slightly dehydrogenated to give neohexene (0.4 turnover after 3 h) (Run 5). Another problem with neohexane lies in its low boiling point which limits the reaction temperature. Although *n*-alkane like decane is far less reactive than cyclooctane in a competitive dehydrogenation,[1a)] decane is too reactive as a solvent. Actually, decenes were formed in a larger amount than COE (Run 6). Other solvents like mesitylene, *t*-$BuCO_2Me$, and *t*-BuOMe hampered the reaction to result in low yields of COE (Runs 7-9). This is probably because the C-H bonds of these solvents oxidatively add to the rhodium center competitively with the substrate C-H bonds although resulting intermediates cannot undergo β-hydride elimination. Coordination of oxygen and scission of the carbon-oxygen bond in the ester or the ether may be other possible factors to reduce the catalytic

Table 1. Dehydrogenation of alkanes in solvents[a]

Run	Substrate	Solvent	Time / h	Conv. / %	Yield[b] / % (Turnover)		
					COE	1,3-COD	Dimers
1	cyclooctane	$(t\text{-BuCH}_2)_2$	1	60	52 (38)	7	1
			3	92	59 (44)	27	6
2	cyclooctane	cyclooctane	1	1.9	1.9 (72)	0	0
3	cyclooctane[c]	$(t\text{-BuCH}_2)_2$	1	55	48 (126)	5	1
			3	90	60 (156)	21	9
4	cyclooctane	1,3,5-tri-*t*-butylbenzene	1	33	32	2	0
			7	92	62	25	4
5	cyclooctane[d]	$t\text{-BuCH}_2\text{CH}_3$	1	14	14	0	0
			3	37	32	1	3
6	cyclooctane	decane[e]	3	28	27 (20)	1	0
7	cyclooctane	mesitylene	3	4	4	0	0
8	cyclooctane	$t\text{-BuCO}_2\text{Me}$[f]	3	5	5	0	0
9	cyclooctane[d]	*t*-BuOMe[f]	3	6	6	0	0
						decenes[g]	
					t-2	*c*-2	others
10	decane[c]	1,3,5-tri-*t*-butylbenzene	1	2	1	0.5	0
			20	30	11	4	13
			48	42	16	5	19
						pentadecenolides[g]	
11	pentadecanolide[c]	$(t\text{-BuCH}_2)_2$	1	34		32 (54)	
			3	53		50 (84)	

[a] Substrate 0.050 cm^3, Solvent 2.5 cm^3, $RhCl(CO)(PMe_3)_2$ 5.04 µmol, 100 °C, irradiated by a high pressure mercury lamp through a Pyrex filter. [b] Based on substrates charged. [c] Rh 1.26 µmol. [d] Reaction at room temperature. [e] Turnovers of 2-*trans*- and 2-*cis*-decenes were 25 and 11, respectively. [f] Brown solid was deposited. [g] Regioisomeric mixtures.

activity.[7] Substrates other than cyclooctane were also dehydrogenated in **1** or **2** to give olefinic compounds (Runs 10 and 11).

In summary, we have demonstrated the examples of inert solvents for the dehydrogenation of alkanes by the $RhCl(CO)(PMe_3)_2$-hν system. This is very important for practical applications of the catalytic C-H activation in a preparative manner.

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7) In the dehydrogenation of neat ethyl acetate by the same catalytic system, a small amount of acetic acid was formed indicating a C-O oxidative addition (unpublished result).

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