

Catalytic C-H activation by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2-h\nu$ system

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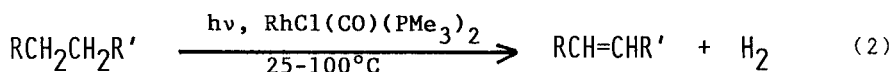
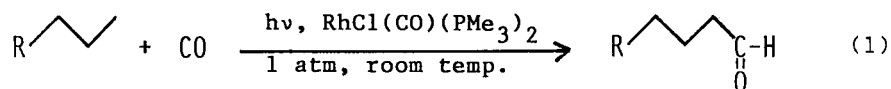
Abstract— $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under irradiation is a powerful catalyst which can functionalize hydrocarbons including alkanes under mild conditions. The reaction with carbon monoxide leads to the formation of the corresponding aldehyde. Alkanes react regioselectively at the terminal methyl group. The reaction of alkanes under inert atmosphere results in the formation of alkenes with a concomitant evolution of dihydrogen. Terminal alkene is obtained from n-alkane in the presence of excess amount of PMe_3 ligand. The irradiation is essential to cause the catalytic C-H activation.

INTRODUCTION

Direct, mild, and selective functionalization of hydrocarbons is one of the major challenges of today's organic chemists to create an entirely new chemical industry based on direct conversion of hydrocarbons. C-H bond activation by transition metal complexes seems to give a clue to solve the problem. However, in spite of the great progress of stoichiometric C-H bond activation with metal complexes (ref. 1), the examples of productive catalytic reactions have been still rare (Table 1) (ref. 2). Moreover, most of them deal with aromatic hydrocarbons. We have recently provided a breakthrough using $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under irradiation; the catalytic system can efficiently activate not only aromatic hydrocarbons but also alkanes with a fascinating regioselectivity (Eq 1-2) (ref. 3). This article will review the catalysis focusing on carbonylation and dehydrogenation.

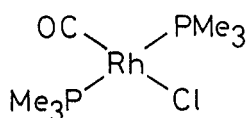
TABLE 1. Direct functionalization of hydrocarbons catalyzed by transition metal complexes

Substrate	Reactant	Catalyst	Irradiation	Product	Turnover	Ref.
PhH	O_2	Pd(II)	no	Ph-Ph	31	2a
PhH	$\text{CH}_2=\text{CH}_2$	Pd(II)+Cu(II)	no	PhCH=CH ₂	5	2b
PhH	$\text{CO}, ^t\text{BuOOH}$	Pd(II)	no	PhCHO	12	2c
PhH	$\text{CH}_2=\text{CH}_2$	Rh(0)	no	PhCH=CH ₂	118	2d
PhH	$\text{Ph}_2\text{C}=\text{C}=\text{O}$	Rh(0)	no	Ph_2CHCOPh	36	2e
PhH	R_3SiH	Ir(I)	no	R_3SiPh	13	2f
PhH	CO	Ir(I), Rh(I)	yes	PhCHO	2	2g
PhH	$^t\text{BuCH}_2\text{NC}$	Fe(0)	yes	$\text{PhC}(=\text{NCH}_2^t\text{Bu})\text{H}$	7	2h
ROCH_3	$^t\text{BuCH}=\text{CH}_2$	Ir(I)	no	$^t\text{BuCH}=\text{CHCH}_2\text{OR}$	12	2i
cyclooctane	none	Ir(I)	yes	cyclooctene, H ₂	8	2j

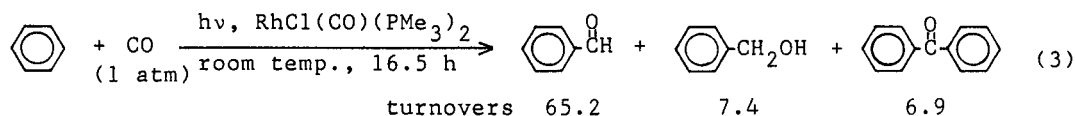


CARBONYLATION

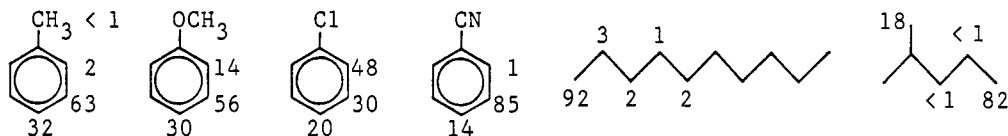
Benzene is photo-carbonylated in the presence of transition metal complexes to give benzaldehyde with simultaneous formation of secondary by-products (mainly benzyl alcohol and benzophenone) (Eq 3). The irradiation is carried out with a high pressure mercury lamp through a Pyrex flask. The catalytic activity largely depends on the structure of catalyst complexes as summarized as follows:



Central metal: Rh >> Ir >> Ru >> Co, Fe, Ni, Pt
 Structure of Rh complexes: RhX(CO)(PR₃)₂ >> other Rh complexes
 As for RhX(CO)(PR₃)₂,
 X: Cl ≅ SCN > F > Br > I > CN ≅ OH
 PR₃: PMe₃ ≅ 1,3,4-trimethylphospholane ≅ 1,3,4-trimethylphospholene > P(CH₂O)₃Me > PET₃ ≅ PBu₃ > P(i-Pr)₃ ≅ PPh₃ ≅ P(OMe)₃ > dppe

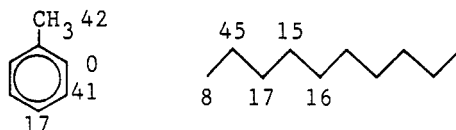


n-Alkane reacts at a similar rate to Eq 3. The catalytic system exhibits quite unique regioselectivity: meta-selectivity for substituted benzenes and terminal selectivity for alkanes (Scheme 1). The aldehydes obtained from alkanes partly undergoes Norrish type II photoreaction to give the terminal olefins of one less carbon than the starting alkanes.



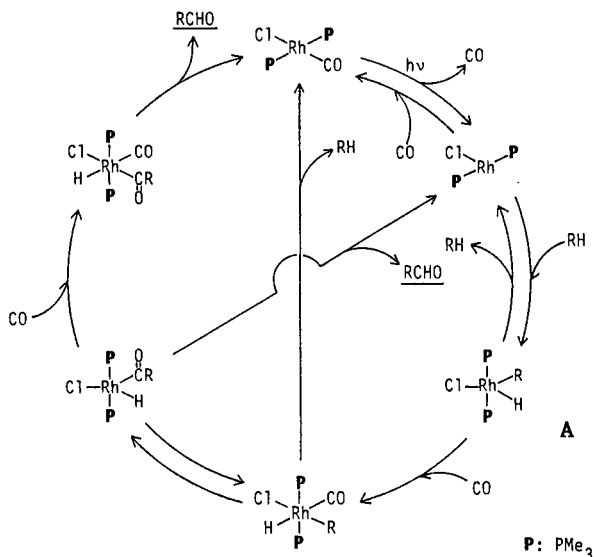
Scheme 1. Regioselectivity of carbonylation by RhCl(CO)(PMe₃)₂-hv system.

The irradiation wavelength influences not only the catalytic activity but also the regioselectivity. The use of a short wavelength cut-off filter (UV-35) results in the loss of terminal selectivity (Scheme 2).

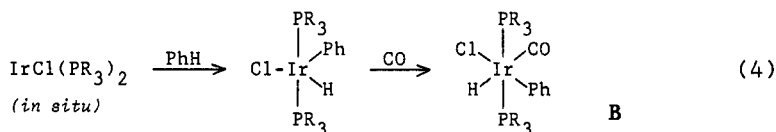


Scheme 2. Regioselectivity obtained with the short-wavelength-cut filter (UV-35).

The proposed mechanism is represented in Scheme 3. The formation of 14 electron highly unsaturated complex, RhCl(PR₃)₂, by the irradiation of Vaska-type rhodium complex has been revealed by Ford et al. (ref. 4). RhCl(PR₃)₂ probably reacts with hydrocarbons to produce a hydridoalkyl (or aryl) complex (A). In fact, the MO calculation by Morokuma et al. has supported the feasibility of this step for the reaction of RhCl(PH₃)₂ with methane (ref. 5). The much higher reactivity of RhCl(PMe₃)₂ for oxidative addition than that of RhCl(PPh₃)₂ has been recently confirmed by Ford et al. through the flash photolysis of these complexes in benzene or cyclohexane (ref. 6). The isolation of oxidative addition product of benzene to an analogous 14 electron complex, IrCl(PR₃)₂ has been reported by Werner (Eq 4) (ref. 7). The resulting hydridophenyl complex is trigonal-bipyramidal. The reaction of the iridium complex with CO resulted in the formation of a hexa-coordinated carbonyl complex (B). Since the alkyl-rhodium bond is supposed to be weaker than the alkyl-iridium one, the rhodium complex corresponding to B probably undergoes CO insertion to give a hydridoacyl complex followed by reductive elimination of an aldehyde.



Scheme 3. Possible reaction mechanism of carbonylation of hydrocarbons by RhCl(CO)(PMe₃)₂.



The unique regioselectivity of the present catalytic system as shown in Scheme 1 is explainable by the thermodynamic stability of hydridoalkyl (or aryl) intermediates on the basis of the following precedents. The facile isomerization of hydridoalkyl (or aryl) rhodium complexes has been reported by Bergman and Jones with Cp*RhR(H)(PMe₃). The

equilibrium ratio of the tolyl complexes is ortho : meta : para = 0 : 2 : 1 (ref. 8). On the other hand, the isomerization of the sec-alkyl complexes to n-alkyl complexes is so fast that only the latter one is detectable (ref. 9). The corresponding sec-alkyl iridium complex, $Cp^*Ir(sec-alkyl)(H)(PMe_3)$ is detectable but is converted to the n-alkyl complex upon heating (ref. 10). The isomerization of sec-alkyl complexes to n-alkyl complexes has also been observed in the decarbonylation of acyl chlorides by Ir(I) complexes (ref. 11).

In contrast, the results of Scheme 2 is possibly ascribed to the kinetic control. The weakest C-H bond in the molecules is preferably activated: benzylic C-H bond in toluene and secondary C-H bond in alkanes. The wavelength dependence of the regioselectivity as seen in Schemes 1 and 2 may imply that the short wavelength light around 300 nm accelerates the isomerization of hydridoalkyl (or aryl) intermediates to a thermodynamically stable isomer.

DEHYDROGENATION

Since transition metal alkyl complexes are usually unstable and easily undergo β -hydride elimination, alkene formation is expected using $RhCl(CO)(PMe_3)_2$ under irradiation via the same intermediate as the carbonylation (A in Scheme 3), followed by β -hydride elimination. As a matter of fact, when an alkane solution of $RhCl(CO)(PMe_3)_2$ is irradiated under dinitrogen or argon, alkene is efficiently formed with a concomitant evolution of dihydrogen (Fig. 1). The turnover rate of cyclooctane dehydrogenation at 29°C is about ten times higher than that of benzene carbonylation. The quantum yield of cyclooctane dehydrogenation reaches 0.16 (365 nm, 75°C). The reverse reaction (hydrogenation) seems to be proceeding simultaneously. In fact, the transfer hydrogenation of cyclohexene with cyclooctane proceeds effectively. The catalyst effect on the activity is similar to that observed in the carbonylation; the highest catalytic activity is achieved by the use of $RhCl(CO)(PMe_3)_2$. However, the terminal selectivity for n-alkane, which is observed in the carbonylation, is not attained in the dehydrogenation. This is partly due to the facile isomerization of terminal alkenes to internal alkenes which is thermodynamically more stable. Terminal alkene is obtained only in the presence of excess amount of PMe_3 (Eq 5). The order of relative reactivity of alkane (cyclooctane > cyclohexane > n-alkanes) is completely the reverse of that reported by Bergman for the oxidative addition to $Cp^*Rh(PMe_3)$ (ref. 12).

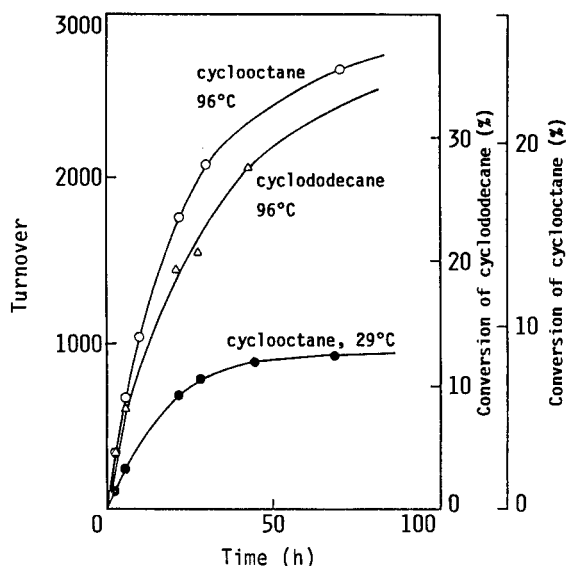
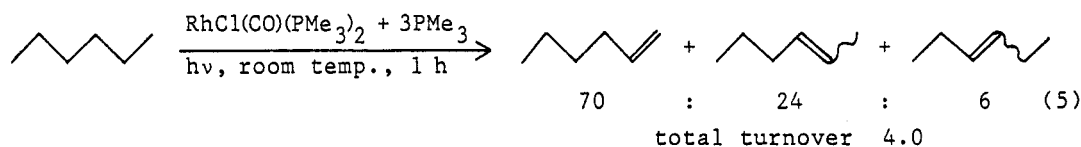


Fig. 1. Time course of dehydrogenation of cycloalkane. $RhCl(CO)(PMe_3)_2$ 0.7 mM.

Although the dehydrogenation of alkane around room temperature is thermodynamically extremely unfavorable, the present dehydrogenation proceeds smoothly even under hydrogen atmosphere (Fig. 2). This strongly indicates that the catalytic cycle involves the photoactivation step to supply the energy required. Recently, Goldman et al. have reported that the catalytic cycle includes one photon, based on the study of photointensity dependence (ref. 13); the irradiation is necessary for the dissociation of CO from $RhCl(CO)(PMe_3)_2$. According to their conclusion, the catalysis should be effected without irradiation if we thermally dissociate L from $RhCl(L)(PR_3)_2$. However, the attempts to carry out the thermal dehydrogenation with $RhCl(PR_3)_2$ have been unsuccessful; although the ligand L can be dissociated thermally from $RhCl(L)(PR_3)_2$ (L = $CH_2=CH_2$, $(H)_2$, N_2) without photolysis, irradiation is absolutely necessary to carry out the catalytic dehydrogenation. The dissociation of N_2 from $RhCl(N_2)(PR_3)_2$ by initial irradiation under argon is also insufficient to realize the thermal reaction (Fig. 3). Finally, it should be interesting to note here that the effect of irradiation conditions (wavelength and intensity) on the catalytic activity is quite different between the dehydrogenation and the carbonylation (ref. 14). Further investigations are necessary to understand the details of the catalysis.

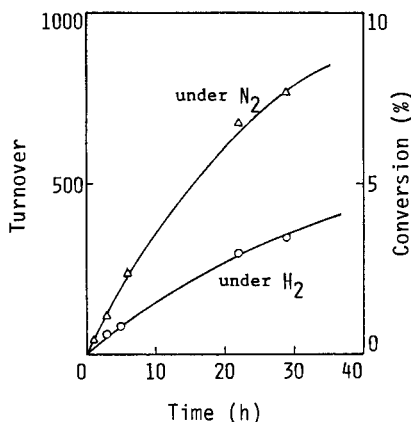


Fig. 2. Dehydrogenation of cyclo-octane by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$. Rh 0.7 mM, room temperature.

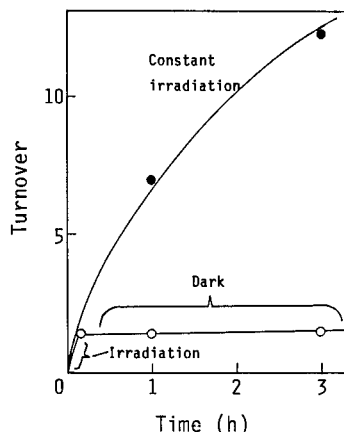


Fig. 3. Dehydrogenation of cyclo-octane by $\text{RhCl}(\text{N}_2)[\text{P}(\text{i-Pr})_3]_2$. Rh 0.7 mM, 96°C, under argon.

OTHER REACTIONS

The $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ -hv system is applicable to various other functionalizations of hydrocarbons: C=C and C≡C insertion, isonitrile insertion, silylation, dehydrogenative coupling etc. The same or a very similar intermediate is presumably responsible for these reactions. As a matter of fact, toluene exhibits the same regioselectivity (ortho : meta : para = 0 : 2 : 1) for both C=C double bond insertion and silylation as for carbonylation. Moreover, a high terminal selectivity is also observed in the acetylene insertion into the C-H bond of n-hexane. The catalytic system will further provide a wide variety of reactions by the combinations of diverse reactants and substrates.

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