Catalytic Intermolecular Hydrogen Transfer with Photogenerated Hydride Transient $CoH[PPh(OEt)_2]_3$

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Pyrex-filtered photoirradiation of a thermally inert complex $CoH[PPh(OEt)_2]_4$ generated a coordinatively unsaturated active hydride species "$CoH[PPh(OEt)_2]_3$" ($CoHP_3$), which catalyzed hydrogen transfer from secondary alcohols to carbonyl compounds, such as ketones. Study of initial reaction-rate dependence of the hydrogen transfer on complex and substrate concentrations indicated that the reaction was initiated by coordination of the carbonyl compounds to the photogenerated $CoHP_3$ species, and these coordination was confirmed by the decay analysis of the transient $CoHP_3$ absorbance observed after laser flash photolysis. In addition, the rate-determining step of the hydrogen-transfer reaction was associated with the hydride transfer to the carbonyl carbon, at the stage of the transformation of hydrido (ketone or aldehyde) cobalt into alkoxo intermediate. Second-order coordination-rate constants k' of aldehydes and ketones to $CoHP_3$ ranged from 10^5 to $10^8\,M^{-1}\,s^{-1}$. The constants k' of aldehydes were considerably larger than those of ketones, where substantial steric repulsion by the bulky substituents introduced in place of the aldehyde hydrogen, was presumed to hinder the $CoHP_3$ approach to the carbonyl group.

Transition-metal hydride complexes have become an important class of compounds in organometallic chemistry, which play a key role in many homogeneous catalytic reactions[1] and have promise also in hydrogen and energy storage systems.[2] Moreover, their photochemical properties[3] have recently received much attention in view of photochemical hydrogen production from water[2a,b] and of photogeneration of highly reactive organometallic fragments.[4]

The hydridophosphonitecobalt(I) complex $CoH[PPh(OEt)_2]_4$ ($CoHP_4$) with an 18-electron configuration is thermally inert. However, Pyrex-filtered photoirradiation of the complex dissociates a phosphonite ligand $PPh(OEt)_2$ (P) from cobalt efficiently without cleavage of the hydrido–cobalt bond, and produces a coordinatively unsaturated transient of the hydride species "$CoH[PPh(OEt)_2]_3$" ($CoHP_3$).[5] The quantum yield for the $CoHP_3$ photogeneration is almost 1.0 at 337 nm.[5b] Furthermore, the species has shown high catalytic activities in double-bond migration of some allylic compounds such as *N,N*-diethylallylamine, and laser flash photolysis displayed the substrate coordination through C=C double bond to the species.[5c]

We now report the photoassisted intermolecular hydrogen transfer from secondary alcohols to carbonyl compounds such as ketones, as an another example of the catalytic reactions by the photogenerated $CoHP_3$ species. Some aspects of this work have appeared in a preliminary communication.[6]

Catalytic transfer hydrogenation using organic compounds as hydrogen sources seems to remain of current interest and secondary alcohols have most often been employed as the sources.[1b,7] In these reactions, homogeneous catalyst have been widely used, such as $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $RuH_2(PPh_3)_4$.[7] However, there were only a few descriptions on the hydrogen transfer catalyzed by photogenerated reactive organometallic species.[8]

Experimental

Materials and General Procedures. The complex $CoH[PPh(OEt)_2]_4$, $CoHP_4$ was prepared by the literature methods.[9] Benzene was treated with concentrated sulfuric acid until thiophene-free. After water washing, it was dried over anhydrous magnesium sulfate, and distilled from sodium under nitrogen. Toluene was purified similarly. For continuous irradiation, a high-pressure mercury lamp (400 W) was used with a Pyrex filter, and reactant solutions were placed at about 45 mm from the lamp.

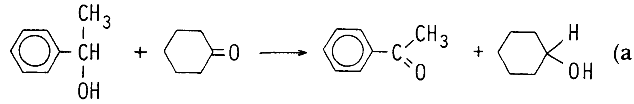
Catalytic Hydrogen Transfer and Product Analyses. Benzene solutions (5 cm^3) of $CoHP_4$ and substrates were degassed by freeze-pump-thaw cycles in a Pyrex Schlenk tube (18 mm$^\phi$). After standing the solutions at 30 °C in the dark or under irradiation to proceed catalytic hydrogen transfer, the reaction mixture was analyzed by Shimadzu GC-8AIT(TCD) and GC-8APF(FID) gas chromatographs with Molecular Sieve 5A, polyethylene glycol 20M, Silicone SE-30, tetrakis-*O*-(2-cyanoethyl)pentaerythritol, and Thermon 3000 columns, together with JEOL model JMS-DX303 GC-mass and JNM-GX-400 NMR spectrometers. Other catalytic reactions described in this paper were conducted similarly.

Laser Flash Photolysis. A Molectron UV-400 nitrogen laser was used for excitation. A right-angle optical system using a 1×1 cm Pyrex cell was employed for the excitation-analysis set-up. The kinetic spectrophotometer and data collection system are described elsewhere.[10] Samples were deaerated by bubbling with argon for 20 min or by several freeze-pump-thaw cycles after transfer of solvent from a reservoir, containing

LiAlH$_4$, using a vacuum line. Second-order rate constants were obtained from the plots of pseudo-first-order rate constants vs. the substrate concentrations, and regarded as accurate to within ca. 10%.

Results and Discussion

Intermolecular Hydrogen Transfer from Secondary Alcohols to Ketones. The CoHP$_4$ complex was mixed with 50-fold moles of cyclohexanone and 1-phenylethanol in benzene, and the solution was irradiated at 30 °C for 8 h by use of a high-pressure Hg lamp with a Pyrex filter. Hydrogen transfer occurred from 1-phenylethanol to cyclohexanone affording acetophenone and cyclohexanol, and virtual stoichiometric relationship was found to hold among these four organic compounds.⁶⁾ The reaction mixture gave



(a)

a value of 0.77 for the molar ratio of cyclohexanol formed to that of cyclohexanone charged. Similar photocatalytic hydrogen transfer was performed also from cyclohexanol to acetophenone (i.e., backward hydrogen-transfer reaction of (a)), and afforded the reaction mixture of comparable composition to that of the forward hydrogen-transfer reaction, indicating equilibration among these alcohols and ketones.⁶⁾ Formation of pinacols and their derivatives was not observed under the present reaction conditions. No other products were detected on the basis of gas chromatography except a small amount of dissociated phosphonite and only trace of molecular hydrogen (less than 2% yield relative to CoHP$_4$).

In the absence of CoHP$_4$, the hydrogen transfer did not proceed even under irradiation, and addition of free phosphonite did not change the situation either. In the dark, the cobalt complex did not cause the hydrogen transfer at 30 °C in benzene at all. Accordingly, the hydrogen transfer of the present system was determined to be photoassisted. In consideration of the fact that the present hydrogen transfer proceeded only under photoirradiation of CoHP$_4$ and ceased immediately upon interruption of irradiation, it was evident that the photogenerated hydride species CoHP$_3$ played an important role in the catalytic cycle of the present hydrogen transfer, similarly to the photoassisted reactions of the olefin double-bond migration reported previously.⁵ᵃ,ᶜ⁾

Dependence of the Hydrogen-Transfer Reaction-Rates on Concentrations of the Cobalt Complex and Substrates. For benzene solutions of 0.82 M†† 1-phenylethanol and cyclohexanone, the initial reaction rate of the hydrogen transfer became larger as the concentration of CoHP$_4$ increased from 0.16× to 0.82×10^{-2} M (Fig. 1). However, in the range above 0.82×10^{-2} M, the initial reaction rate did not change so much upon the further increase in the CoHP$_4$ concentration, and the rate seemed to approach one asymptotic value. This finding was attributed to the saturated photogeneration of the hydride CoHP$_3$ species due to total absorption of the incident light. Similar phenomenon was noticed also in the conversion of cyclohexanone to cyclohexanol after 4 h.

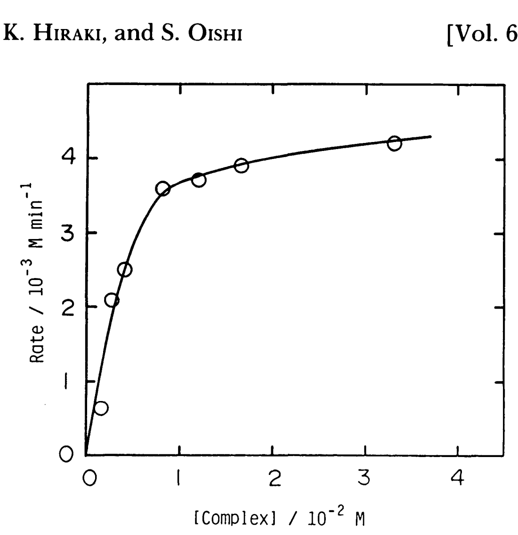


Fig. 1. Dependence of the initial rate of hydrogen transfer on the CoH[PPh(OEt)$_2$]$_4$ concentration. 1-Phenylethanol, 0.82 M; cyclohexanone, 0.82 M.

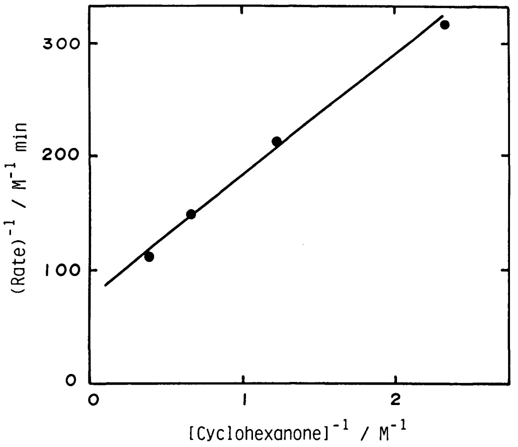


Fig. 2. Double reciprocal plots of the initial reaction rate against the cyclohexanone concentration. CoH[PPh(OEt)$_2$]$_4$, 0.0165 M; 1-phenylethanol, 0.82 M.

At the fixed concentrations of CoHP$_4$ (1.65×10^{-2} M) and 1-phenylethanol (0.82 M), we studied concentration effects of the cyclohexanone charged, and found that the reciprocal initial reaction rate bore a linear relationship with the reciprocal

$$\left[\frac{d[Y]}{dt}\right]^{-1}_{t=0} = \frac{1}{V} + \frac{K_m}{V} \times [S]^{-1}_{t=0},$$

S=cyclohexanone, t=time, Y=cyclohexanol,

V=1.28×10^{-2} M min^{-1}, K_m=1.32 M, Correlation coefficient=0.997

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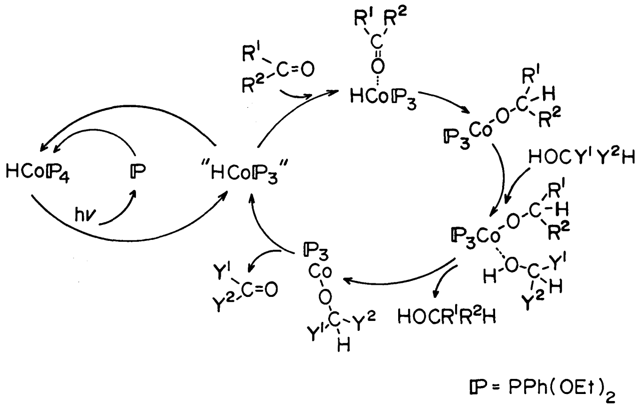
†† 1 M=1 mol dm^{-3}.

concentration of the cyclohexanone charged (Fig. 2). On the contrary, the initial reaction rate was practically independent of the concentration of 1-phenylethanol charged, as shown in Fig. 3, where the concentration ranged from 0.4 to 2.5 M.

As for the mechanism of the present hydrogen transfer, we propose the reaction pathway, which involves initial coordination of ketone to the CoHP$_3$ species photogenerated and the hydride transfer to the carbonyl carbon in ketone, forming an alkoxo intermediate. Subsequent reaction of the intermediate takes place with reactant alcohol to release product alcohol converted from the charged ketone, accompanied by transformation into another intermediate with the alkoxo group of the reactant alcohol. The latter intermediate is expected to afford product ketone and to regenerate the catalytic hydride CoHP$_3$ species through β-hydrogen elimination. As mentioned above (Fig. 2), the linear relationship was observed on the double reciprocal plots of the initial reaction rates and the concentrations of the ketones charged, in sharp contrast to the case of the alcohols where their concentrations did not affect significantly the initial reaction rates in the concentration range under discussion. By analogy with the Michaelis–Menten model,[11] this result supported coordination equilibrium of ketones to CoHP$_3$ in our proposed reaction pathway. Moreover, pulsed laser photolysis of CoHP$_4$ was performed in the presence of some substrates used in this study, and confirmed ketone coordination to the photogenerated CoHP$_3$ species (vide infra).



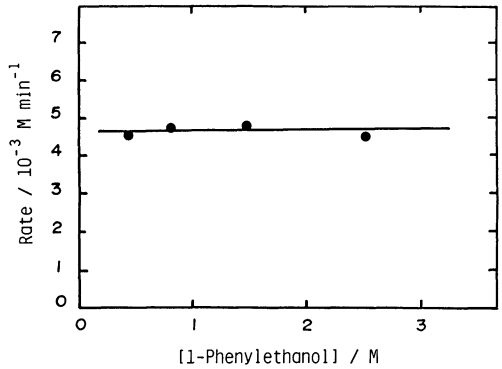


Fig. 3. Dependence of the initial reaction rate on the 1-phenylethanol concentration. CoH[PPh(OEt)$_2$]$_4$, 0.0165 M; cyclohexanone, 0.82 M.

Hydrogen Transfer to 4-Alkyl-Substituted Cyclohexanones. 4-Alkyl-substituted cyclohexanones were employed as hydrogen acceptors in the photoassisted hydrogen-transfer reaction with the cobalt complex, to study stereoselectivity in reduction of the carbonyl groups. The hydrogen-transfer reaction of 1-phenylethanol with 4-methylcyclohexanone in benzene for 4 h gave 4-methylcyclohexanols with the cis/trans isomer ratio of about 2.1 in a 65% conversion, whereas similar reaction of neat 2-propanol showed the cis/trans ratio of 2.4 with the 87% conversion. For 4-*t*-butylcyclohexanone, the hydrogen-transfer reaction of 1-phenylethanol in benzene proceeded slowly to give 2.2 and 19% for the cis/trans value and the conversion, respectively. Free-energy difference between cis and trans 4-*t*-butylcyclohexanols has been described to be about 0.5 kcal mol^{-1},[12] which led to a value of 0.43 for the cis/trans ratio in the thermodynamically equilibrated state at 30 °C. It was determined that the present photoassisted hydrogen transfer with CoHP$_4$ afforded kinetically controlled product composition rather than thermodynamically controlled one, and preferred formation of thermodynamically less stable cis isomers. During the course of the probable transformation of hydrido(4-alkylcyclohexanone)cobalt species to cis and trans (4-alkylcyclohexyloxy)cobalt through hydride transfer to the carbonyl carbon, steric

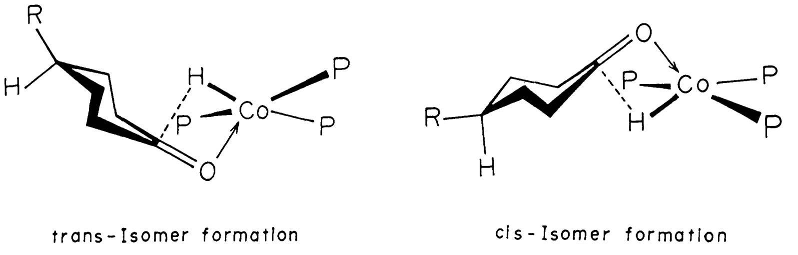


Fig. 4. Formation of trans and cis 4-substituted cyclohexanols.

approach control was presumed to prefer less sterically hindered pathway effectively, which afforded axial i.e. cis cyclohexanols.

Hydrogen Transfer to *p*-Substituted Benzaldehydes. In the hope to obtain some further clues to the present reaction mechanism, we performed the hydrogen transfer from neat 2-propanol to some *p*-substituted benzaldehydes, and studied substituent effect on the initial formation rates of the corresponding benzyl alcohols. Figure 5 shows good linear relationship of the logarithmic formation rates with the respective Hammett substituent constants $\sigma_p{}^+$. The reaction constant (the gradient of the linear relationship) ρ and the correlation coefficient were 1.348 and 0.997, respectively. Positive reaction constant ρ implys that the rate was enhanced by withdrawal of electron density from the reaction site. In connection with the above-described observation of the kinetically controlled hydrogen transfer to 4-alkyl-substituted cyclohexanones, this fact led us to conclude that the important rate-determining step was the hydride transfer to the carbonyl carbon with partial positive charge, at the stage of the transformation of hydrido(aldehyde or ketone)cobalt into alkoxocobalt intermediate.[13] Subsequent reaction of the alkoxo intermediate with secondary reactant alcohols was assumed to be fast, in conformity with the finding that the initial hydrogen-transfer rate was not dependent apparently on the concentration of secondary alcohols charged (Fig. 3).

Laser Flash Photolysis and Substrate Coordination to CoHP$_3$. Laser flash photolysis of CoHP$_4$ was performed at 337 nm using a nitrogen laser in the presence of some substrates, such as cyclohexanone and 1-phenylethanol in benzene at room temperature. In the time-resolved absorption spectra, we monitored the decay of the transient bands of photogenerated CoHP$_3$ at 580 and 760 nm, due to recombination with free phosphonite and to substrate coordination. Table 1 summarizes the second-order coordination-rate constants k' of these and some related substrates.[5c,14]

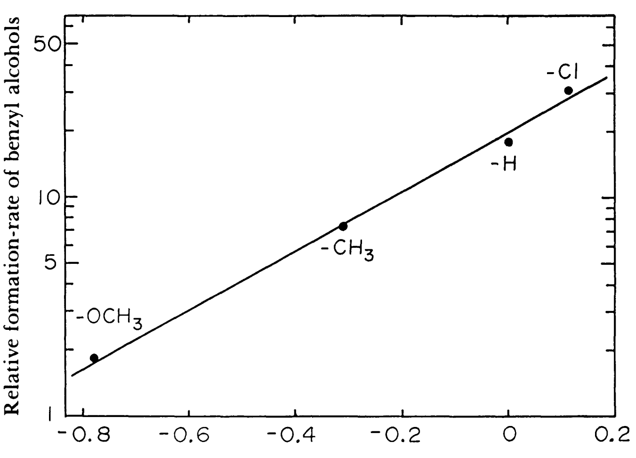


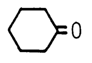
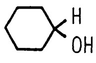
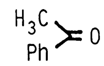
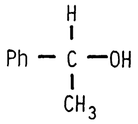
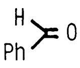
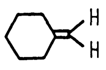
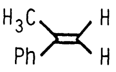
Fig. 5. Plots of the logarithmic formation rate of *p*-substituted benzyl alcohols against Hammett $\sigma_p{}^+$. CoH[PPh(OEt)$_2$]$_4$, 5X10^{-3} M; *p*-substituted benzaldehyde, 0.2 M; solvent, 2-propanol; temperature, 30 °C.

$$-\frac{d[\mathrm{CoHP_3}]}{dt} = k[\mathrm{CoHP_3}][\mathrm{P}] + k'[\mathrm{CoHP_3}][\mathrm{Substrate}]$$

$$\mathrm{P{=}PPh(OEt)_2},\ k{=}1.4{\times}10^8\ \mathrm{M^{-1}\,s^{-1}}$$

The constants k' of ketones and aldehydes ranged from 10^5 to 10^8 M^{-1} s^{-1}, whereas those of the secondary alcohols were very small and undetermined explicitly. Therefore, this result confirmed the ketone coordination to the photogenerated CoHP$_3$ species, in the above-described reaction pathway concerning the photoassisted hydrogen transfer with CoHP$_4$. Moreover, Table 1 shows the constants k' of aldehydes were considerably larger than those of ketones. When the photogenerated CoHP$_3$ species approach the carbonyl groups in these compounds, interaction of the species was initiated with the HOMO of the groups, which expand mainly over the sp^2-hybrid plane,[15] as illustrated in Fig. 6. In the case of aldehydes, the CoHP$_3$ species can approach the carbonyl group easily through the less hindered side including the aldehyde hydrogen on the hybrid plane. However, in the case of ketones, substantial steric repulsion by the bulky

Table 1. Second-Order Rate Constants k' (M^{-1} s^{-1}) for Coordination

	8.6X10^5		Negligible
	3.2X10^5		Negligible
	1.6X10^8		9.4X10^6
	1.1X10^8		9.1X10^6

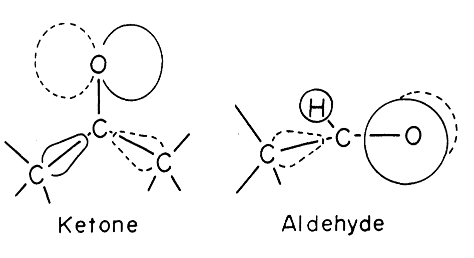


Fig. 6. Pictorial representation of the HOMO (n) orbitals of the carbonyl groups.

substituents introduced in place of the aldehyde hydrogen, was presumed to hinder the CoHP$_3$ approach to the carbonyl group. Steric factor was described previously to be dominant in the magnitude of the constants k' for aliphatic amines.[14]

It is noteworthy also that methylenecyclohexane showed a comparable value of the rate constant to that of 2-phenylpropene, whereas the constant of cyclohexanone was larger than that of acetophenone by a factor of ca. 2.7. In the cases of the former two substrates of olefins, the CoHP$_3$ species was attracted by the olefinic π-bond electrons and approached the axial site over the sp^2-hybrid plane of the two double-bonded carbons. On the other hand for the ketones, the species approached the HOMO expanded mainly over the sp^2-hybrid plane of the carbonyl groups, and steric factor was assumed to work in this planar approach process.

Concluding Remarks

Photogenerated hydride transient CoHP$_3$ catalyzed intermolecular hydrogen transfer from secondary alcohols to carbonyl compounds such as ketones. The catalytic reaction was initiated by coordination of the carbonyl compounds to CoHP$_3$. The rate-determining step was associated with the hydride transfer to the carbonyl carbon, at the stage of the transformation of hydrido(ketone or aldehyde)cobalt into alkoxo intermediate.

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13) The present authors did not agree with one-step addition model of the hydrido–cobalt bond to the carbonyl group through possible four-centered transition state, but supported stepwise addition model, i.e. coordination of the group to cobalt via oxygen atom and subsequent hydride transfer to the carbonyl carbon, in view of the following matters; (1) Observed double-reciprocal linear relationship between the initial hydrogen-transfer rates and ketone concentrations charged (Fig. 2), indicating coordination equilibrium of ketones to CoHP$_3$. (2) Spatial distribution of HOMO in the carbonyl groups (Fig. 6).

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