CHEMISTRY LETTERS, pp. 1157 - 1160, 1984.

HYDROGEN-TRANSFER FROM ALCOHOLS TO KETONES CATALYZED BY PHOTOGENERATED ACTIVE SPECIES FROM A STABLE HYDRIDOPHOSPHONITECOBALT(I) COMPLEX

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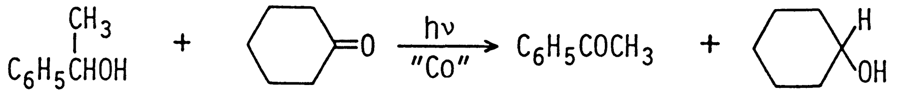
Pyrex-filtered irradiation of a thermally inert complex $[CoH\{PPh(OEt)_2\}_4]$ generated a coordinatively unsaturated active hydrido species "$CoH\{PPh(OEt)_2\}_3$", which catalyzed hydrogen-transfer from secondary alcohols to ketones. The reaction was "photoassisted" rather than "true photocatalytic".

Photoreactivity of transition-metal hydrido complexes$^{1)}$ seems to be one of current topics in organometallic chemistry, in view of photochemical hydrogen production from water$^{2)}$ and of low-temperature photogeneration of reactive organometallic fragments$^{3)}$ for some catalytic reactions$^{4)}$ and syntheses of new complexes.$^{5)}$ Recently, we$^{6)}$ reported that irradiation of a thermally inert complex $[CoH\{PPh(OR)_2\}_4]$ dissociated a phosphonite ligand from cobalt efficiently without cleavage of the hydrido-cobalt bond to produce a coordinatively unsaturated hydrido species "$CoH\{PPh(OR)_2\}_3$", and that the species catalyzed isomerization of 3-phenylpropene. In the course of our investigation on the catalytic activities of the species, it was found that the species catalyzed hydrogen-transfer from 1-phenylethanol to cyclohexanone yielding acetophenone and cyclohexanol. To our knowledge, the present work is the first definite example of intermolecular hydrogen-transfer from alcohol, catalyzed by the photogenerated species from stable transition-metal hydrido complexes.$^{7-9)}$



(1)

The complex $[CoH\{PPh(OEt)_2\}_4]$ (ε:6400 at λ_{max} 344 nm) (0.1 mmol) was added to a benzene solution (5 cm^3) of cyclohexanone (5.0 mmol) and 1-phenylethanol (5.0 mmol), and the solution was irradiated externally at 30 °C at a distance of *ca.* 45 mm from the center of a 400 W high-pressure Hg lamp equipped with a Pyrex filter. The complex caused the hydrogen-transfer from 1-phenylethanol to cyclohexanone under irradiation. Virtual stoichiometric relationship was found to hold among four organic compounds in Eq. 1. No other products were detected on the basis of gas chromatography, except a small amount of dissociated phosphonite and only trace of molecular hydrogen (*ca.* 0.002 mmol). Formation of pinacols and their derivatives was not observed in the presence of the complex under the present conditions. The conversion of cyclohexanone to cyclohexanol was evaluated from the ratio of the quantity of cyclohexanol formed to that of cyclohexanone charged, and was about 77% after irradiation of 8 h. When we added 1, 2, and 4 mol of free $PPh(OEt)_2$ relative to 1 mol of the complex, conversions were decreased to 55, 34, and 16%, respectively. The addition of free $PPh(OEt)_2$ accelerated probably recombination process of the coordinatively unsaturated hydrido species and the free phosphonite to suppress the reaction of the species with cyclohexanone or 1-phenylethanol.

In the absence of the complex, the hydrogen-transfer did not occur under irradiation, and the addition of free phosphonite did not change the situation either. In the dark, the cobalt complex did not cause the hydrogen-transfer at all at 30 °C for 8 h, and even under benzene reflux the conversion was only 3% after 4 h.

Irradiation-period dependency of the hydrogen-transfer is demonstrated by curve R in Fig. 1. After the mixture of the complex, 1-phenylethanol, and cyclohexanone was irradiated for 1 h, irradiation was stopped (P in Fig. 1) and the mixture was left in the dark at 30 °C for 20 h. The hydrogen-transfer was ceased completely during the period in the dark. Upon reirradiation at Q, the hydrogen-transfer proceeded again, showing only slight decrease in the catalytic activity of the complex during the dark period (curve S). Therefore, the hydrogen-transfer of the present system was virtually "photo-assisted" rather than "true photocatalytic".[10] The photogenerated hydrido species was assumed to have a comparatively short lifetime due to easy recombination with the photodissociated phosphonite. This was responsible for the immediate drop of the reaction rate of hydrogen-transfer observed upon interruption of irradiation.

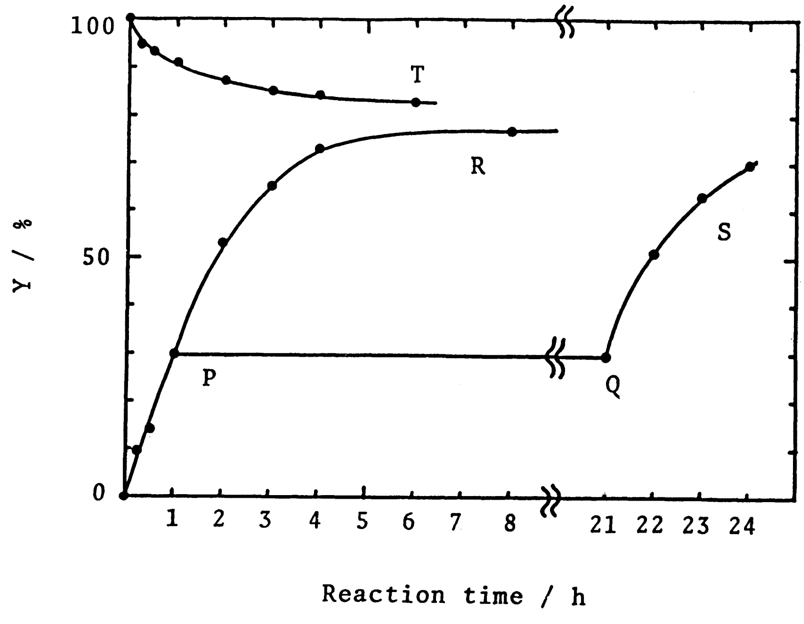


Fig. 1. Time-dependent hydrogen-transfer by $[CoH\{PPh(OEt)_2\}_4]$.

Y: (cyclohexanol)/{(cyclohexanol) + (cyclohexanone)}

R, S: reaction of cyclohexanone (1 mol dm^{-3}) and 1-phenylethanol (1 mol dm^{-3})

T: reaction of cyclohexanol (1 mol dm^{-3}) and acetophenone (1 mol dm^{-3})

$[CoH\{PPh(OEt)_2\}_4]$: 0.02 mol dm^{-3}

P-Q: dark period, 20 h

When a benzene solution of cyclohexanone (4.0 mmol), 1-phenylethanol (4.0 mmol), and the complex (0.08 mmol) was irradiated for 8 h, cyclohexanol and acetophenone were formed in equimolar amounts of *ca*. 3.08 mmol. Then, the irradiated solution was combined with another solution of cyclohexanone (4.0 mmol) and 1-phenylethanol (4.0 mmol), and additional irradiation for 4 h increased the quantities of cyclohexanol and acetophenone to *ca*. 4.0 mmol. These increases indicated that a large portion of the catalysis was still living even after the first irradiation for 8 h.

Curve T in Fig. 1 illustrates reverse hydrogen-transfer from cyclohexanol to acetophenone yielding cyclohexanone and 1-phenylethanol, and suggests the equilibration among these ketones and alcohols after prolonged reaction-times. While Adkins *et al*.11) described oxidation potentials of the reacting ketones which led to a value of 29 for the equilibrium constant of Eq. 1 at 30 °C, our estimated value from Fig. 1 was about 16.

Thus, the present study demonstrates the hydrogen-transfer from secondary alcohols to ketones, catalyzed by the facilely photogenerated active species from the stable hydridocobalt(I) under mild conditions. A plausible mechanism for the present hydrogen-transfer involves (1) photogeneration of the coordinatively unsaturated hydrido species, (2) successive addition of the hydrido species to the carbonyl group in ketone, forming an alkoxo intermediate, and (3) reaction of the intermediate with reactant alcohol to release product alcohol converted from the initial ketone, accompanied by transformation into another intermediate with the alkoxo group of reactant alcohol. The latter intermediate was expected to afford product ketone and to regenerate the catalytic hydrido species through β-hydrogen elimination.

It is notable that the cobalt complex (0.4 mmol) was irradiated for 6 h with cyclohexanone (0.2 mmol) alone to give about 0.06 mmol of cyclohexanol.12) The coordinatively unsaturated hydrido species would react with cyclohexanone to form the alkoxo intermediate, which gave cyclohexanol by reaction with another hydrido species.13) However, the alkoxo intermediate was not isolated owing to its easy decomposition through β-hydrogen elimination. On the other hand, photoirradiation of the complex (0.1 mmol) with 1-phenylethanol (5.0 mmol) for 6 h yielded molecular hydrogen (*ca*. 0.09 mmol) and acetophenone (*ca*. 0.09 mmol).12) In these reactions between the complex and one substrate under irradiation, cyclohexanol or acetophenone was formed very slowly, in sharp contrast to the case of the reaction of the complex with both cyclohexanone and 1-phenylethanol.

We are grateful to Dr. M. Iwamoto and Dr. S. Kagawa for help in measurement of molecular hydrogen.

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(Received April 27, 1984)