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Studies on Catalysis by Molten Metals

X. Hydrogen Transfer Reactions between Alcohols and Ketones on Liquid Indium Catalyst

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Hydrogen transfer reactions between alcohols and ketones were studied on liquid indium catalyst by using a pulse reaction technique, and a plausible reaction model is proposed to explain the experimental results including deuterium isotope effects. Further, the stereoselectivity observed in the transfer hydrogenation of methylcyclohexanones and the selectivities observed in the transfer hydrogenation of unsaturated ketones are discussed in terms of the proposed model.

INTRODUCTION

Many studies have been made of the transfer hydrogenations on metal oxides and metals such as palladium, nickel, and copper, and the reaction mechanisms have also been clarified to some extent (*1–9*). However, a comprehensive understanding of the reaction mechanism seems to be difficult on account of the complexity of the reaction over the solid catalyst. An adequate selection of catalyst and the use of a refined experimental technique seem to be necessary to clarify the reaction mechanism.

In this connection, the application of the liquid metal as the catalyst for the transfer hydrogenation looks promising. Earlier works of this series (*10–19*) have demonstrated the superiority of the use of the liquid metal catalysts in obtaining reproducible experimental results and in elucidating the reaction mechanism. Experimental techniques for the study of the catalysis by liquid metals have been fully developed in the authors' laboratory (*15, 16, 18*), and the experimental results including the kinetic deuterium isotope effect have been shown to afford useful data in discussing the reaction mechanism in terms of quantum chemistry (*17, 19*).

Thus, liquid indium has been employed in the present work as a catalyst for the transfer hydrogenations between alcohols and ketones including unsaturated ketones. The experimental results as well as the discussion on the reaction mechanism are reported in this paper.

EXPERIMENTAL METHODS

Materials

Indium of 99.999% purity was used as a source of the molten metal catalyst. All the reagents, except 4-methyl-3-cyclohexenone and 2-cyclohexenone, were obtained commercially. 4-Methyl-3-cyclohexenone and 2-cyclohexenone were prepared by the usual methods (*20, 21*). Ethanol-d_1 (CH_3CH_2OD) and ethanol-d_6

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TABLE 1

Experimental Results of the Hydrogenation of Ketones on Liquid Indium Catalyst

Substrate	Reaction temp (°C)	Injected amount (μl)	Conversion (%)
Acetone	460	0.2	1.4
	460	0.4	0.50
	460	0.6	0.35
2-Butanone	460	0.2	2.0
	460	0.4	1.1
	460	0.6	0.68
	405	0.2	1.1
	405	0.4	0.68
	405	0.6	0.48

(CD_3CD_2OD) used for the measurements of kinetic isotope effects were obtained from E. Merck Darmstadt.

Apparatus and Procedures

Details of the microreactor employed in this work has been described previously (*18*). In the transfer hydrogenation, the reactant, i.e., the mixture of hydrogen donor compound and the acceptor compound, was injected into a stream of purified helium gas (2.3 atm) which serves as carrier [in the hydrogenation reactions, purified hydrogen gas (2.1 atm) was used as a carrier gas]. The mass spectrometric analysis of the reaction products of the transfer hydrogenation between CH_3CH_2-OD and cyclopentanone was made with a JEOL 06H GC-mass spectrometer. Infrared spectra of the reaction products of transfer hydrogenation between CH_3CH_2-OD and acetone were obtained with a Perkin-Elmer Model 337 grating infrared spectrometer.

RESULTS

Hydrogenation of Ketones

Results of hydrogenation of acetone and 2-butanone on liquid indium catalyst are presented in Table 1. As shown in Table 1, conversion of acetone or 2-butanone is small but appreciable. Although the thermochemical data (*22*) predict the small equilibrium conversion for the hydrogenation of ketones (or aldehydes), the temperature dependence of the conversion of 2-butanone indicates that the reaction is kinetically controlled because the conversion at 405°C is smaller than that at 460°C. If the reaction is thermodynamically controlled, the conversion should become larger as the temperature becomes lower because the reaction is exothermic (*22*).

Transfer Hydrogenation between Ethanol and 2-Butanone

Results of transfer hydrogenation between ethanol and 2-butanone are shown in Fig. 1. The data on product analyses as well as the material balance showed that when the mixture of ethanol and 2-butanone is passed over the indium catalyst, the

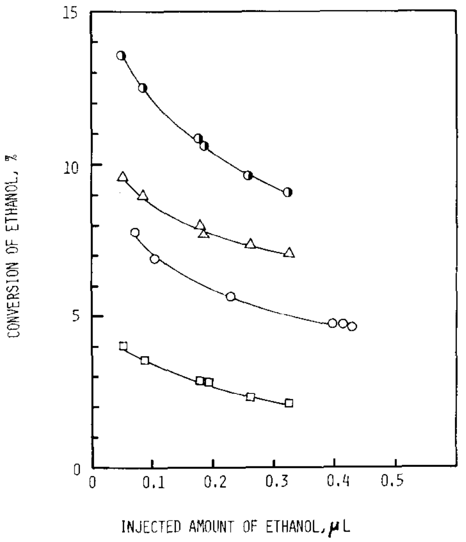
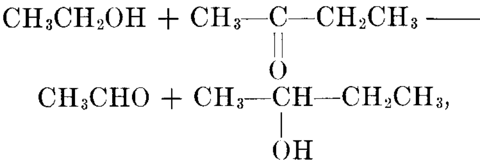


FIG. 1. Experimental results of transfer hydrogenation between ethanol and 2-butanone. Composition of reactant: ethanol:2-butanone = 0.54:0.46 (mol ratio). Reaction temperature, 460°C. (◑) Total conversion of ethanol in ethanol-2-butanone reactant system (X_t); (△) conversion of ethanol due to the transfer hydrogenation (X_1); (□) conversion of ethanol due to the dehydrogenation (X_2); (○) conversion of ethanol in the one component reactant system (ethanol) (X_{2s}).

following two reactions [Eqs. (1) and (2)] take place;



$$CH_3CH_2OH + CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2CH_3 \longrightarrow CH_3CHO + CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_2CH_3, \quad (1)$$

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2. \quad (2)$$

Therefore, the total conversion (X_t) of ethanol in the ethanol-2-butanone binary reacting system was considered to be the sum of conversion for Eqs. (1) and (2), i.e., $X_t = X_1 + X_2$. The open circles in Fig. 1 represent the conversion (X_{2s}) of ethanol in a separate experiment for the dehydrogenation of ethanol. It must be pointed out from Fig. 1 that $X_t > X_{2s}$, though $X_{2s} > X_2$. This means that ethanol is effectively acting as a hydrogen donating reagent. The same relations were observed not only for ethanol-2-butanone system, but also for ethanol–cyclopentanone system, ethanol–methylcyclohexanone system, and 1-propanol–methylcyclohexanone system.

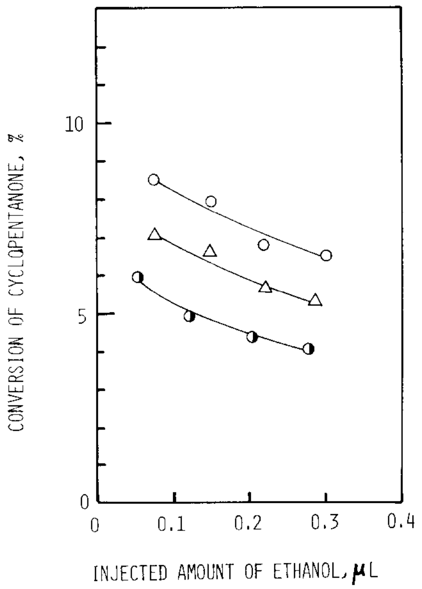


FIG. 2. Kinetic isotope effects in the transfer hydrogenation between ethanol and cyclopentanone. Composition of reactant: ethanol:cyclopentanone = 0.49:0.51 (mol ratio). (○) CH_3CH_2OH–cyclopentanone system; (△) CH_3CH_2OD–cyclopentanone system; (◑) CD_3CD_2OD–cyclopentanone system.

TABLE 2

Result of Mass Spectrometric Analysis of Cycolpentanol Produced by the Transfer Hydrogenation between CH_3CH_2OD and Cyclopentanone

m/e	Relative intensity
28	1000
29	51
32	256
41	68
43	63
44	114
57	210

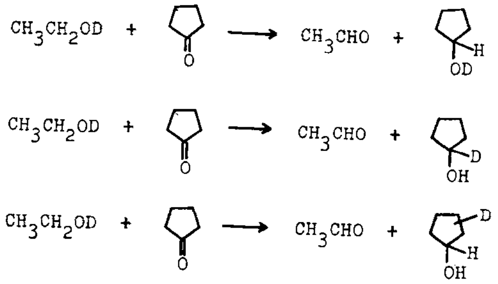
Kinetic Isotope Effects for the Transfer Hydrogenation between Ethanol and Cyclopentanone

Experimental results of kinetic isotope effects in the transfer hydrogenation between ethanol and cyclopentanone are shown in Fig. 2. Figure 2 shows that $X_{d_0} > X_{d_1} > X_{d_6}$, where X_{d_0}, X_{d_1}, and X_{d_6} are conversions of cyclopentanone when CH_3CH_2OH, CH_3CH_2OD, and CD_3CD_2OD are used as hydrogen donors, respectively. More quantitatively, we get from Fig. 2 the average kinetic isotope effects for the transfer hydrogenation as follows;

$$X_{d_0}/X_{d_1} = 1.23, \quad (3)$$

$$X_{d_1}/X_{d_6} = 1.33. \quad (4)$$

In the reaction between the deuterioethanol and cyclopentanone, an additional experiment was carried out. Namely, the products of the reaction between CH_3CH_2OD and cyclopentanone were treated with large excess of CH_3CH_2OH, and mass spectrometric analysis of the resulting products was carried out. The experimental results are summarized in Table 2. The comparison of the results shown in Table 2 with the mass spectra of cyclopentanol in the literature (*23*) shows that the majority of the cyclopentanol molecule did not contain deuterium. This means that only C_5H_9OD was produced in the transfer hydrogenation between CH_3CH_2OD and cyclopentanone, and the produced C_5H_9OD was converted to C_5H_9OH by the treatment with excess alcohol. Therefore, the reaction between CH_3CH_2OD and cyclopentanone should be expressed as (5a), and the reactions (5b) and (5c) must be excluded;



(5a)

(5b)

(5c)

Further, in the infrared spectra of the product of reaction between CH_3CH_2OD and acetone, absorption peaks for the C–D stretching vibration were not observed. This provides the other evidence for the validity of the above-mentioned scheme.

Transfer Hydrogenation of Methylcyclohexanones

The data on *cis*- or *trans*-selectivity in the transfer hydrogenation of methylcyclohexanones are presented in Table 3. As shown in Table 3, *trans*-alcohols are preferentially produced in the reactions of both 2-methylcyclohexanone and 4-methylcyclohexanone, whereas *cis*-alcohol is predominantly formed in the reaction of 3-methylcyclohexanone. The effects of alcohols (donors) to the stereoselectivity seem to be relatively small. Namely, it can be seen in Table 3 that different hydrogen donors yield essentially the same *cis*- or *trans*-selectivity in the transfer hydrogenation of 2-methylcyclohexanone.

TABLE 3

Results of Transfer Hydrogenation of Methylcyclohexanones on Liquid Indium Catalyst at 460°C

Hydrogen		*cis*- %	*trans*- %
Acceptor	Donor		
2-Methylcyclohexanone	Ethanol	44.0	56.0
	3-Hexanol	43.4	56.6
3-Methylcyclohexanone	1-Propanol	58.2	41.8
4-Methylcyclohexanone	1-Propanol	44.5	55.5

Reaction of Hydrocarbons

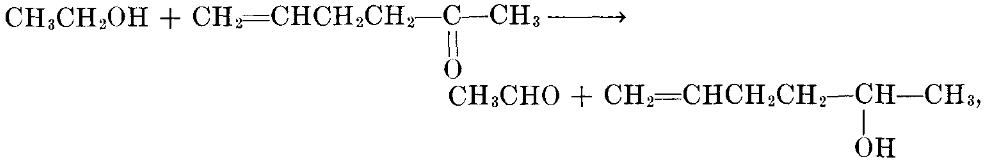
Concerning the reactions listed in Table 4, no sign of catalysis of liquid indium was recognized. Liquid indium was found to be inactive for the dehydrogenation, the hydrogenation, and the transfer hydrogenation of hydrocarbons. In the reaction of alcohol–olefin binary system, only the dehydrogenation of alcohol was observed, the hydrogen transfer from alcohol to olefin was not observed, and the conversion of the dehydrogenation of alcohol was found to be little affected by the presence of olefins.

Transfer Hydrogenation of γ,δ- and β,γ-Unsaturated Ketones

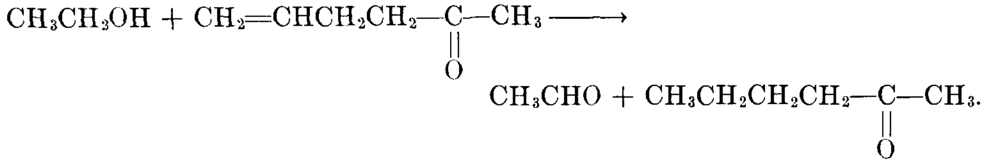
As mentioned above, the transfer hydrogenation between alcohol and olefin was not catalyzed by the liquid indium catalyst. This result is in marked contrast to the fact that the transfer hydrogenation between alcohol and ketone was readily catalyzed.

Thus, it is of interest to investigate the mode of the hydrogen transfer from alcohol to unsaturated ketones which have both $>C=O$ and $>C=C<$ groups.

The experimental results of transfer hydrogenation between ethanol and 5-hexen-2-one are presented in Fig. 3. The figure shows that only the reaction (6a) was catalyzed by the liquid indium catalyst, and the reaction (6b) was not catalyzed;



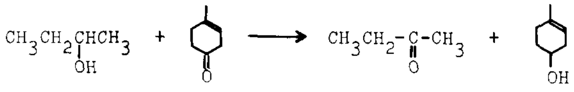
$$\mathrm{CH_3CH_2OH + CH_2{=}CHCH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3CHO + CH_2{=}CHCH_2CH_2-\underset{\underset{OH}{|}}{CH}-CH_3,} \tag{6a}$$



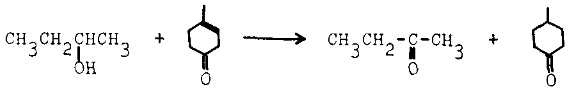
$$\mathrm{CH_3CH_2OH + CH_2{=}CHCH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3CHO + CH_3CH_2CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3.} \tag{6b}$$

The $>C=O$ group of 5-hexen-2-one was selectively hydrogenated by ethanol, whereas the $>C=C<$ group was not hydrogenated.

Similarly, the $>C=O$ group of 4-methyl-3-cyclohexenone (a β,γ-unsaturated ketone) was selectively hydrogenated by 2-butanol, i.e., only the reaction (7a) was catalyzed by liquid indium but the reaction (7b) was not catalyzed;



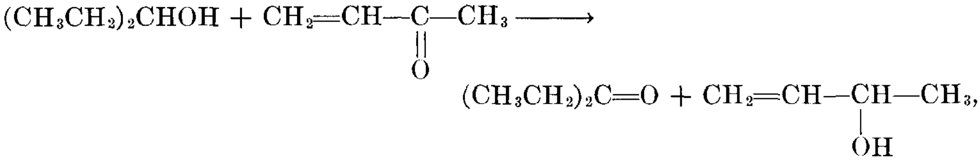
(7a)



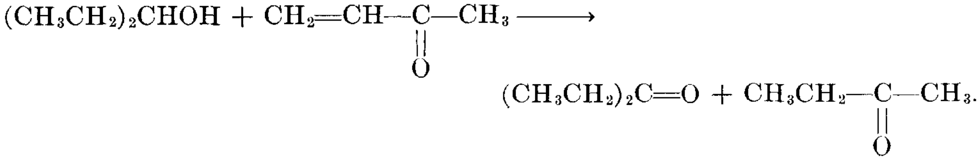
(7b)

Transfer Hydrogenation of α,β-Unsaturated Ketones

As shown in Fig. 4, in the transfer hydrogenation between 3-pentanol and 3-buten-2-one, both of the following reactions were found to occur on the liquid indium catalyst;



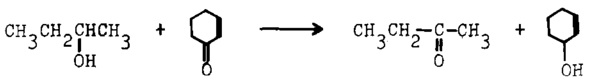
$$\mathrm{(CH_3CH_2)_2CHOH + CH_2{=}CH-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow (CH_3CH_2)_2C{=}O + CH_2{=}CH-\underset{\underset{OH}{|}}{CH}-CH_3,} \tag{8a}$$



$$\mathrm{(CH_3CH_2)_2CHOH + CH_2{=}CH-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow (CH_3CH_2)_2C{=}O + CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3.} \tag{8b}$$

Namely, both $\gt C{=}C\lt$ and $\gt C{=}O$ groups in the 3-buten-2-one molecule can be hydrogenated by 3-pentanol.

Similarly, the data given in Table 5 show that both of the following reactions occurred on the liquid indium catalyst;


(9a)


(9b)

that is, both $\gt C{=}C\lt$ and $\gt C{=}O$ groups in the 2-cyclohexenone molecule can be hydrogenated by 2-butanol.

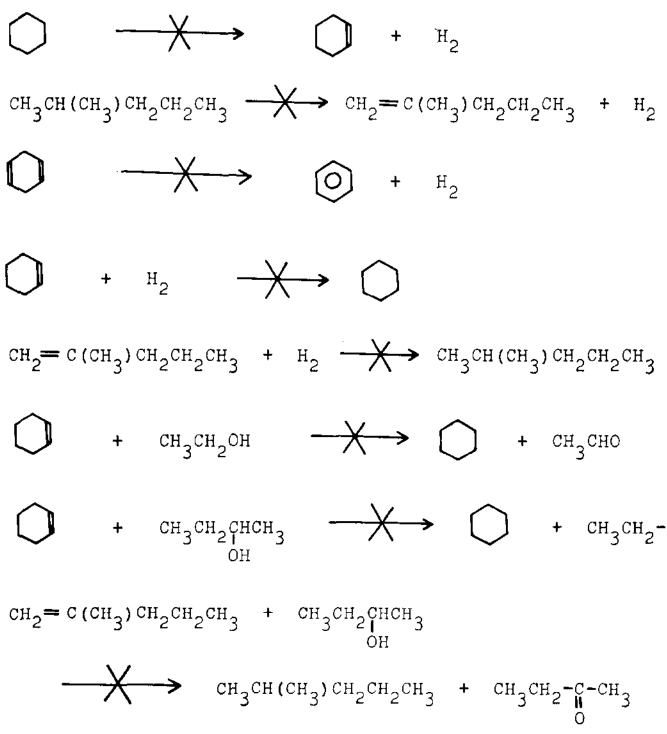
Thus, it can be said that not only the $\gt C{=}O$ group but also the $\gt C{=}C\lt$ group of α,β-unsaturated ketone can be hydrogenated by alcohols on the liquid indium catalyst.

Reaction of 2-Propen-1-ol

Results of the reaction of 2-propen-1-ol are given in Fig. 5. The figure shows that the isomerization [Eq. (10)] is accompanied with the dehydrogenation and the formation of saturated alcohol [Eq. (11)]

TABLE 4

REACTIONS OF HYDROCARBONS STUDIED ON LIQUID INDIUM CATALYST



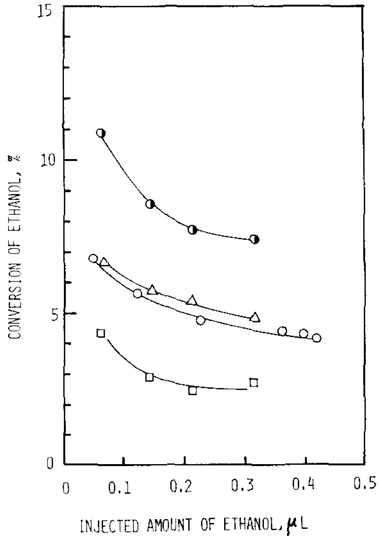


FIG. 3. Experimental results of transfer hydrogenation between ethanol and 5-hexen-2-one at 460°C. Composition of reactant; ethanol: 5-hexen-2-one = 0.51:0.49 (mol ratio). (◑) Total conversion of ethanol in ethanol-5-hexen-2-one reactant system; (△) conversion of ethanol due to the transfer hydrogenation; (□) conversion of ethanol due to the dehydrogenation; (○) conversion of ethanol in the one component reactant system (ethanol).

on the liquid indium catalyst:

$$CH_2{=}CHCH_2OH \longrightarrow CH_3CH_2CHO, \quad (10)$$

$$CH_2{=}CHCH_2OH \xrightarrow{H_2} CH_3CH_2CH_2OH. \quad (11)$$

DISCUSSION

Mechanism of Transfer Hydrogenation between Alcohol and Ketone

The first question to be answered in the transfer hydrogenation between alcohol and ketone on the liquid indium catalyst is which of the indirect hydrogen transfer path [Eqs. (12a), (12b)] and direct hydrogen transfer path [Eq. (13)] is the real one:

i. Indirect hydrogen transfer,

$$RR'CHOH \longrightarrow RR'CO + H_2, \quad (12a)$$

$$R''R'''CO + H_2 \longrightarrow R''R'''CHOH. \quad (12b)$$

ii. Direct hydrogen transfer,

$$RR'CHOH + R''R'''CO \longrightarrow RR'CO + R''R'''CHOH. \quad (13)$$

In the indirect hydrogen transfer, the hydrogen acceptor (ketone) is successively hydrogenated by hydrogen produced by the dehydrogenation of alcohol [Eq. (12a)]. On the other hand, in the direct hydrogen transfer, the donor (alcohol) interacts directly with the acceptor (ketone) on the liquid indium catalyst.

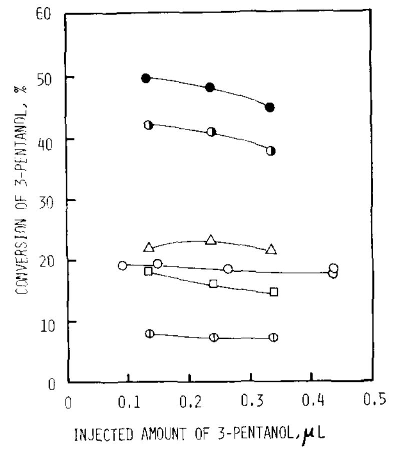


FIG. 4. Experimental results of transfer hydrogenation between 3-pentanol and 3-buten-2-one at 460°C. Composition of reactant: 3-pentanol: 3-buten-2-one = 0.49:0.51 (mol ratio). (●) Total conversion of 3-pentanol in 3-pentanol-3-buten-2-one reactant system; (◑) conversion of 3-pentanol due to the transfer hydrogenation; (△) conversion of 3-pentanol due to the transfer hydrogenation [Eq. (8a)]; (□) conversion of 3-pentanol due to the transfer hydrogenation [Eq. (8b)]; (⦶) conversion of 3-pentanol due to the dehydrogenation in 3-pentanol-3-buten-2-one reactant system; (○) conversion of 3-pentanol in the one component reactant system (3-pentanol).

TABLE 5

Result of Transfer Hydrogenation between 2-Cyclohexenone and 2-Butanol on Liquid Indium Catalyst at 460°C[a]

Product	Yield (%)	Selectivity (%)
2-Cyclohexenol	17.5	85
Cyclohexanone	3.0	15

[a] Composition of reactant; 2-cyclohexenone: 2-butanone = 0.39:0.61 (mol ratio). Injected amount of reactant, 5 μl.

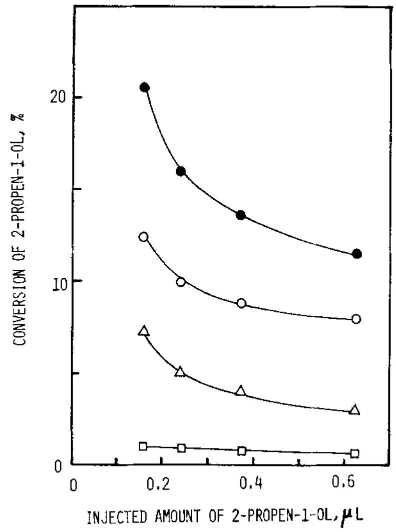
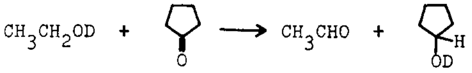


FIG. 5. Experimental results of the reaction of 2-propen-1-ol at 460°C. (●) Total conversion of 2-propen-1-ol; (○) conversion of 2-propen-1-ol due to the dehydrogenation; (△) conversion of 2-propen-1-ol due to the isomerization to propanal; (□) conversion of 2-propen-1-ol due to the formation of saturated alcohol.

According to the experimental results, the direct hydrogen transfer path seems to take place. In spite of much lower partial pressure of hydrogen in the transfer hydrogenation ($\lesssim 0.01$ atm) than that in the hydrogenation of ketones (2.1 atm), the conversion of ketone in the former reaction is considerably higher than the conversion in the latter reaction (Fig. 1, Table 1). If the indirect hydrogen transfer path is the main route of the transfer hydrogenation, the second step of the reaction path, i.e., Eq. (12b), should be very slow and the conversion should be much smaller than the observed value.

The mode of the direct transfer hydrogenation between alcohol and ketone can be understood by the aid of the reaction model given in Fig. 6. In this model, H^1 and H^2 atoms of the hydrogen donor (alcohol) interact with O and C atoms of $\begin{matrix}\diagdown\\ C{=}O\\ \diagup\end{matrix}$ group in the hydrogen acceptor (ketone), respectively. According to this model, CH_3CH_2OD should react with cyclopentanone in the following manner:



(14)

This is consistent with the experimental results [Eq. (5a)]. Further, the model predicts that both H^1 and H^2 atoms in alcohols are responsible for the deuterium isotope effects. The reason is that, according to the model, the transfer step of both H^1 and H^2 atoms participate in the rate controlling step. The observed isotope effects are summarized in Fig. 2, and Eqs. (3) and (4). Since secondary isotope effects are generally smaller than primary isotope effects (*24*), the observed results can easily be understood on the basis of the reaction model.

As shown in Fig. 1, the conversion of transfer hydrogenation is larger than that of the dehydrogenation of ethanol. Similarly, the total conversion of ethanol in the reaction of ethanol–2-butanone system is greater than the conversion observed in the separate dehydrogenation of ethanol. The reaction model shown in Fig. 6 can qualitatively explain these results as follows: In the dehydrogenation of ethanol, the alcohol molecule interacts with the catalyst surface and decomposes unimolecularly to acetaldehyde and hydrogen gas on the surface (*15*, *17*, *18*). On the other hand, in the transfer hydrogenation, as can be seen in Fig. 6, the alcohol molecule interacts with both the catalyst

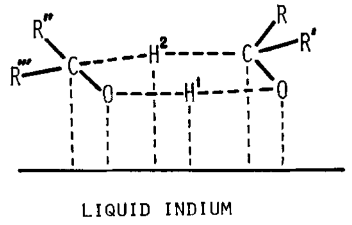


FIG. 6. Model of the transfer hydrogenation between alcohol and ketone on liquid indium catalyst.

surface and the ketone. Therefore, it is probable that the activation energy of transfer hydrogenation would be lower than that of the dehydrogenation of alcohol by the additional interaction.

In the studies of transfer hydrogenations of ketones on metal oxides (*2–5*), metal alkoxides have been considered to be the intermediate of the reaction. On liquid indium, however, the metal alkoxide seems not to be the intermediate of the transfer hydrogenation on the basis of the following data:

i. Both hydrogen atoms of O–H and C–H bonds of alcohol are responsible for the deuterium isotope effects (Fig. 2).

ii. In the gaseous products of the dehydrogenation of CH_3CH_2OD (or $(CH_3)_2CHOD$) HD was selectively found, and the formation of D_2 was negligible [Table 1 in (*18*)].

Stereoselectivities of Transfer Hydrogenation of Methylcyclohexanones

The hydrogen transfer model shown in Fig. 6 can explain the stereoselectivity observed in the transfer hydrogenation of methylcyclohexanones. The application of the model to methylcyclohexanones gives the models shown in Fig. 7. In this figure, two kinds of reaction models are drawn. They are the models of the equatorial attack and the axial attack. Taking into consideration of the experimental results shown in Table 3, it is highly probable that every methylcyclohexanone molecule is attacked axially by the alcohol molecule. According to Morrison and Mosher (*25*), cyclohexanone derivatives are axially attacked by such small reagents as $LiAlH_4$, $NaBH_4$, or CH_3MgBr, because the torsional strain between 2,6-axial hydrogens and the reagent is larger than the steric strain between 3,5-axial hydrogens and the reagent. The preferential axial attack of alcohol to methylcyclohexanone on liquid indium can be explained in the same manner as above. The above discussions are based on the assumption that the effect of catalyst on the stereoselectivities of transfer hydrogenation of methylcyclohexanones is small. This assumption seems to be valid on liquid indium catalyst, because alcohols (or ketones) can be considered to be weakly adsorbed on liquid indium (~10 kcal/mol) (*15, 16*), and adsorbed alcohol behaves like 2-dimensional gas (*15, 16*). The weak adsorption energy is in accord with the absence of the effect of catalyst on the stereoselectivities.

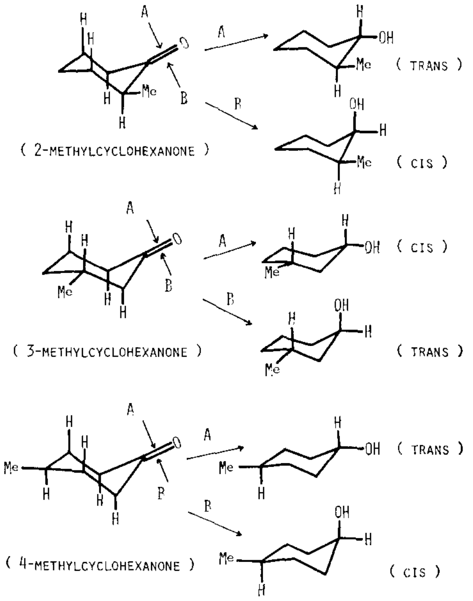


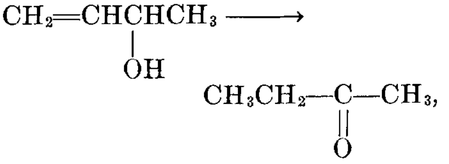
FIG. 7. Models of transfer hydrogenation of methylcyclohexanones. (A) Axial attack; (B) equatorial attack.

Mechanism of Transfer Hydrogenation of Unsaturated Ketones

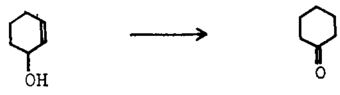
The mechanism of transfer hydrogenation between γ,δ- or β,γ-unsaturated ketone and alcohol is thought to be the same as that of the reaction between saturated ketone and alcohol, because the $\diagdown C{=}O \diagup$ group of the unsaturated ketone was selectively hydrogenate by alcohol whereas the

$>C{=}C<$ group was not hydrogenated. Further, the experimental results obtained for ethanol-5-hexen-2-one system (Fig. 3) are similar to that obtained for the ethanol–2-butanone system (Fig. 1). Thus, there is no reason to deny the application of the same mechanism as shown in Fig. 6 to the transfer hydrogenation of $>C{=}O$ group in unsaturated ketone [Eqs. (8a) or (9a)].

As to the mechanism of the formation of saturated ketone [Eqs. (8b) or (9b)], sufficient data to discuss details of the reaction mechanism are not available. Therefore, only a part of the reaction mechanism is given below. As shown in Eq. (10), 2-propen-1-ol can isomerize to 1-propanol under the same reaction conditions as that of the transfer hydrogenation. Therefore, at least a part of 2-butanone or cyclohexanone can be considered to be formed by the isomerization of 3-buten-2-ol or 2-cyclohexenol, respectively:



$$\underset{\displaystyle OH}{CH_2{=}CHCHCH_3} \longrightarrow CH_3CH_2-\underset{\displaystyle \overset{\|}{O}}{C}-CH_3, \qquad (15)$$



(16)

We must mention, however, that a part of 2-butanone or cyclohexanone may be formed by the 1,4-additions to the 3-buten-2-one or 2-cyclohexenone, respectively, because 1,4-addition to conjugated carbonyls is a well-known process in organic chemistry (*26*).

As shown in Fig. 5, the conversion of 2-propen-1-ol to 1-propanol is small compared with the conversion of the dehydrogenation or the isomerization to propanal. This means that the following disproportionation reaction is hardly catalyzed by the liquid indium catalyst;

$$CH_2{=}CHCH_2OH + CH{=}CHCH_2OH \longrightarrow CH_3CH_2CH_2OH + CH_2{=}CHCHO. \qquad (17)$$

Thus, it can be said that the $>C{=}C<$ group of 2-propen-1-ol is difficult to hydrogenate with 2-propen-1-ol on liquid indium.

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