

Transfer Hydrogenation and Transfer Hydrogenolysis

VIII. Hydrogen Transfer from Amines to Olefins Catalyzed by Heterogeneous and Homogeneous Catalysts

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It was found that Pd-carbon, Pd-asbestos, and Pd-black have high catalytic activity in the hydrogen transfer from indoline to cycloheptene. $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$, IrCl_3 , $(\text{NH}_4)_2\text{PdCl}_4$, and $\text{RhH}(\text{PPh}_3)_4$ also showed high activity. The hydrogen-donating ability of organic compounds in the hydrogen transfer reaction catalyzed by Pd-carbon decreased in the order: indoline > formic acid > tetrahydroquinoline > piperidine > pyrrolidine > cyclohexene > *N*-methylpyrrolidine > di-*n*-propylamine > *n*,*L*-limonene > 1,2-dihydronaphthalene, etc. Though monoenes were hydrogenated efficiently, 1,3- and 1,5-cyclooctadiene were reduced to cyclooctene in high selectivity. The initial rate of the hydrogen transfer from indoline to cycloheptene was proportional to the amine concentration at first and then became independent of the amine concentration. The rate showed a maximum when the olefin concentration was varied. This result indicates the poisoning effect of the olefin.

INTRODUCTION

It has been reported (1) that in catalytic transfer hydrogenation and transfer hydrogenolysis, hydroaromatics such as cyclohexene, tetraline, and limonene, alcohols, formic acid, arylaldehydes (2), and *N*-methylformamide (2) can be used as hydrogen sources, and that palladium catalysts are most active in most cases in heterogeneous catalysis.

In the systematic investigation of hydrogen-donating ability of organic compounds in which olefins and $\text{RhCl}(\text{PPh}_3)_3$ were used as hydrogen acceptors and a catalyst, respectively, we found that amines and cyclic ethers are excellent hydrogen donors (3-5).

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This study was undertaken to investigate heterogeneous transfer hydrogenations, especially the ones using amines as hydrogen sources, by comparing them with homogeneous transfer hydrogenations.

EXPERIMENTAL

Materials

Palladium asbestos, palladium carbon, palladium black, iridium trichloride, ruthenium trichloride, rhenium pentachloride, ammonium palladous chloride, potassium chloroplatinate, nickel bromide, and stannous chloride were purchased and used without purification. Dichlorobis(triphenylphosphine)ruthenium(II) (6), hydridotetrakis(triphenylphosphine)rhodium(I) (7), chlorotris(triphenylphosphine)rhodium(I) (8), hydridocarbonyltris(triphenylphos-

phine)rhodium(I) (9), dichlorobis(triphenylphosphine)platinum(II) (10), tetrakis(triphenylphosphine)platinum(O) (11), dichlorobis(triphenylphosphine)palladium(II) (12), dichlorobis(tri-*n*-butylphosphine)palladium(II) (13), dicyanobis(triphenylphosphine)palladium(II) (14), dibromobis(triphenylphosphine)nickel(II) (15), diiodobis(triphenylphosphine)nickel(II) (15), dibromobis(tri-*n*-butylphosphine)nickel(II) (16), dibromobis(triphenylphosphine)cobalt(II) (17), and dichlorobis(triphenylphosphine)iron(II) (18) were prepared by the methods reported in the literature. Olefins, ethers, and hydrocarbons were purified by distillation over metallic sodium. Amines, except for piperadine, were distilled. Piperadine was recrystallized from benzene. Alcohols were dried with molecular sieves after distillation. All solvents were purified by distillation and dried by the usual methods.

TABLE 1
Catalytic Activity^a

Catalyst	Reaction time (hr)	Yield of cycloheptane (%)
50% Pd-asbestos	1	95
5% Pd-carbon	1	90
	1.5	61 ^b
	1.5	24 ^c
Pd-black	1	87
RuCl ₃ (PPh ₃) ₃	1	78
RhCl ₃ ·2H ₂ O ^d	4	73
IrCl ₄ ^d	4	63
(NH ₄) ₂ PdCl ₆ ^e	4	56
RhH(PPh ₃) ₄	4	51
RhCl(PPh ₃) ₃ ^d	4	4

^a Cycloheptene (0.25 *M*), indoline (0.50 *M*), and the designated catalyst were heated in toluene at 120°C. The concentration of catalysts was 10 g/liter for metallic palladium catalysts and 25 mM for other catalysts.

^b This reaction was carried out at 90°C.

^c This reaction was carried out at 90°C in a vessel which had been sealed under an atmosphere of air.

^d This catalyst did not dissolve completely.

^e Metallic mirror was formed.

An Example of Transfer Hydrogenation

Cycloheptene (24 mg, 0.25 mmol), indoline (60 mg, 0.50 mmol), and 5 wt% palladium carbon (10 mg) were put into a Pyrex glass tube which had been sealed at one end, and the total volume of the solution was made 1.0 ml by the addition of toluene as a solvent. The tube was sealed under vacuum with liquid nitrogen. The sealed tube was heated for 1 hr with continuous oscillation in the polyethylene glycol bath kept at 90 ± 1°C. The reaction mixture was submitted glc analysis in which 25 μl of cyclohexane was used as an internal standard. A 2 m × 6 mm stainless steel column packed with 25% of 1,2,3-tris(2'-cyano-ethoxy)propane on Celite 545 was used. The amount of indole and indoline was measured by the use of a 2 m × 6 mm column packed with 10% diethylene glycol succinate on Diasolid L and of dibenzyl ether as an internal standard.

Other transfer hydrogenations were carried out in a similar way.

In the reactions at temperatures higher than 140°C, a silicone-oil bath was used instead of the polyethylene glycol bath.

An Example of Kinetic Runs

Four samples, prepared by the method described above, were heated at 90 ± 1°C for 20, 30, 40, and 50 min, respectively. The reaction mixtures were submitted to the glc analysis.

RESULTS AND DISCUSSION

Unless otherwise noted, all the experiments in this study were carried out under the following conditions. A hydrogen donor (0.50 *M*), a hydrogen acceptor (0.25 *M*), and a catalyst in a solvent were sealed in a Pyrex glass tube under a vacuum and heated with oscillation. The presence of air in the vessel retarded the transfer hydrogenation as shown in Table 1, and the

reproducibility and the rate of the reaction were lower without the agitation.

1. Catalytic Activity

In the reaction system in which indoline, cycloheptene, and the designated catalyst in toluene were heated at 120°C, the catalytic activity of several catalysts was investigated. (Table 1). The concentration of complex and salt catalysts was 25 mM and the amount of heterogeneous catalysts was 10 g/liter of the solution. In these concentrations, the amount of metallic palladium in palladium complexes is about 5.3 times as much as that in 5 wt% palladium carbon (Pd/C). Under this reaction condition, the activity of the catalysts decreased in the following order: 50 wt% palladium asbestos > Pd/C > palladium black > RuCl₂(PPh₃)₃ > RhCl₃·2H₂O > IrCl₃ > (NH₄)₂PdCl₄ > RhH(PPh₃)₄ > RhCl(PPh₃)₃. When (NH₄)₂PdCl₄ was used, metallic mirror was formed, but the metal collected showed no catalytic activity. Under the same reaction condition, PtCl₂(PPh₃)₂, PtCl₂(PPh₃)₂ + SnCl₂·H₂O (0.25 M), Pt(PPh₃)₄, K₂PtCl₆, ReCl₅, PdCl₂(PPh₃)₂, Pd(CN)₂(PPh₃)₂, PdCl₂(PBuⁿ)₂, RhH(CO)(PPh₃)₃, RhCl(CO)(PPh₃)₂, RuCl₃·H₂O, NiBr₂(PPh₃)₂, NiI₂(PPh₃)₂, NiBr₂(PBuⁿ)₂, NiBr₂, CoBr₂(PPh₃)₂, and FeCl₂(PPh₃)₂ did not catalyze the transfer hydrogenation.

As all the heterogeneous palladium catalysts had high activity, Pd/C was used in any experiment described hereafter as a representative of heterogeneous catalysts.

2. Hydrogen-Donating Ability

The hydrogen-donating ability of several organic compounds was evaluated by heating them with cycloheptene and Pd/C in toluene. From the results summarized in Table 2, it was found that the ability decreased in the order: indoline > formic acid > tetrahydroquinoline > piperidine >

pyrrolidine > cyclohexene > *N*-methylpyrrolidine > di-*n*-propylamine > *D,L*-limonene > 1,2-dihydronaphthalene > *N*-methylpiperazine > tri-*n*-butylamine > *N,N'*-dimethylpiperazine. Benzylamine, cyclohexylamine, tetraline, 1-propanol, 1-butanol, 2-propanol, cyclohexanol, dioxane, tetrahydrofuran, tetrahydrothiophene, benzaldehyde, *N*-methylformamide, and 2-pyrrolidone did not give hydrogen even in the reaction at 180°C. This result shows that some *N*-unsubstituted cyclic amines have high hydrogen-giving activity and that secondary amines generally donate hydrogen more strongly than tertiary amines. Especially, indoline reduced the olefin

TABLE 2
Donor Activity with Cycloheptene^a

Hydrogen donor	Reaction temp. (°C)	Reaction time (hr)	Yield of cycloheptane (%)
Indoline	180	2	100
	160	3	100
	110	1	65
	70	0.5	16
	60	14	81
Formic acid	110	1	25
Tetrahydroquinoline	180	2	100
	160	3	89
	120	2	2
Piperidine	180	2	100
	160	3	45
Pyrrolidine	180	2	87
Cyclohexene	180	2	84
<i>N</i> -Methylpyrrolidine	180	2	21
Di- <i>n</i> -propylamine	180	2	17
Piperadine	180	2	16
<i>D,L</i> -Limonene	180	2	15
1,2-Dihydronaphthalene	180	2	14
<i>N</i> -Methylpiperazine	180	2	8
Tri- <i>n</i> -butylamine	180	2	7
<i>N,N'</i> -Dimethylpiperadine	180	2	5
Tri- <i>n</i> -propylamine	180	2	4
<i>n</i> -Propylamine	180	2	3
Morpholine	180	2	1

^a Cycloheptene (0.25 M), the designated hydrogen donor (0.50 M), and Pd/C (10 g/liter) were heated in toluene.

TABLE 3
Quantitative Relation^a

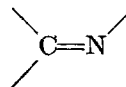
Charged cycloheptene, <i>M</i>	Composition of reaction mixture, <i>M</i>			
	Cyclo- heptane	Cyclo- heptene	Indole	Indoline
0	0	0	0.04	0.48
0.25	0.12	0.13	0.11	0.39
0.50	0.14	0.36	0.13	0.36
1.00	0.08	0.93	0.09	0.42
1.50	0.04	1.48	0.03	0.49

^a Cycloheptene, indoline (0.50 *M*), and Pd/C (10 g/liter) were heated in the solvent at 90°C for 1 hr.

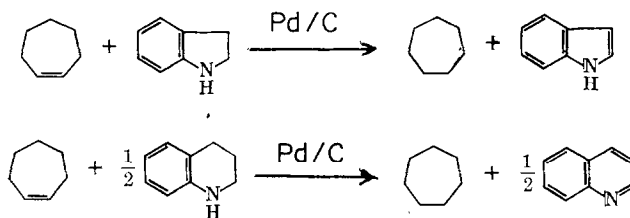
even at 60°C. Primary amines hardly showed the activity.

The quantitative relation in the reaction between cycloheptene and indoline (Table 3) is summarized as follows. (1) The amount of indole was equal to that of cycloheptene within experimental error; (2) the total amount of the survived donor and the dehydrogenated donor equaled the

amount of the charged donor within experimental error; (3) the total amount of the cycloheptane and cycloheptene was equal to the amount of charged cycloheptene. In a similar reaction in which 0.50 *M* tetrahydroquinoline, 0.25 *M* cycloheptene, and the catalyst were heated at 160°C for 3 hr in toluene, 0.22 *M* cycloheptane and 0.12 *M* quinoline were obtained. Cycloheptadienes which would be formed by the disproportionation of cycloheptene were negligibly detected in any case. In spite of the report that in the presence of Raney nickel (19-21) or metallic palladium (22), *prim*- and *sec*-amines undergo dehydrogenation to form the



bond and then other amines are added to the imino bond, these results show that hydrogen atoms transferred from indoline or tetrahydroquinoline to cycloheptene without considerable side reactions as follows.



When piperidine and pyrrolidine were used, no low-boiling dehydrogenation products, such as pyridine and pyrrole, were detected. It has been reported that 1-piperidine and 1-pyrrolidine are so unstable as to undergo rapid trimerization in the absence of amines (23, 24) and addition reaction in the presence of amines (21, 22). Therefore, it is inferred that dehydrogenation intermediates might react further to give products of higher molecular weight which could not be detected by glc analysis.

The driving force for piperidine and pyrrolidine to donate hydrogen may not be due to aromatization, because aromatization products, such as pyridine and pyrrole, were not detected in the reaction mixture.

Formic acid also effectively donated hydrogen atoms to the olefin, and evolved gas which perhaps contains carbon dioxide.

Cyclohexene gave hydrogen fairly well, while tetraline did not. This is in contrast to the homogeneous system catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ in which the latter reduces

olefins rather well while the former hardly does (4). Cyclohexene seems to have high hydrogen-donating ability characteristically in the heterogeneous palladium catalysis (1).

It is noteworthy that primary and secondary alcohols and cyclic ethers which showed high donor activity in homogeneous transfer hydrogenations (3,4,25,26) did not reduce cycloheptene at all. This might suggest that the affinity of these oxygen compounds to the heterogeneous catalyst is much smaller than that of the olefin. This reasoning may be supported by the poisoning effect of the olefin and the solvent effect described later.

3. Hydrogen Acceptors

It has been reported that in the hydrogenation of olefins by molecular hydrogen in the presence of Pd/C, the rate-determining step is not the absorption of olefins to the catalyst but the transfer of adsorbed hydrogen to olefins (27). According to the report, the rate of the hydrogenation of cycloolefins by molecular hydrogen decreases in the order: cyclohexene > cycloheptene > cyclopentene > 1,5-cyclooctadiene > cyclooctene. However, in this transfer hydrogenation, the conversion to hydrogenation products diminished in the order (Table 4): 1,5-cyclooctadiene > cycloheptene > cyclohexene > cyclopentene > cyclooctene. Therefore, the step that the activated hydrogen originated from indoline transfers to olefins, is speculated not to be rate-determining. The dependence of the rate on the concentration of cycloheptene and indoline, which will be described later, suggests that the relative strength of the adsorption of hydrogen donors and olefins greatly influences the rate.

It is worthy of notice that 1,3- and 1,5-cyclooctadiene were hydrogenated readily and that the main product was cyclooctene, for these dienes were scarcely reduced

TABLE 4
Transfer Hydrogenation of Olefins^a

Olefin	Product	Yield (%)
α -Methylstyrene	Cumene	97
1-Octene	<i>n</i> -Octane	47
1,5-Cyclooctadiene	Cyclooctane	9
	Cyclooctene	37
	1,3-Cyclooctadiene	5
Cycloheptene	Cycloheptane	45
Cyclohexene	Cyclohexane ^b	43
1,3-Cyclooctadiene	Cyclooctane	6
	Cyclooctene	29
Cyclopentene	Cyclopentane	29
Cyclooctene	Cyclooctane	24

^a Indoline (0.50 *M*), Pd/C (10 g/liter), and the designated olefin (0.25 *M*) were heated in anisole at 90°C for 1 hr.

^b No benzene was detected.

in homogeneous transfer hydrogenations (3,4,25,26). Even in the reduction of cyclohexene, benzene was negligibly detected. This indicates that the hydrogen-giving power of indoline is much stronger than that of cyclohexene. In the case of 1-octene, the isomerization to internal olefins also occurred. Carbonyl compounds, such as propionaldehyde and acetone, seem to react with indoline, because these compounds were consumed and no alcohols were obtained.

4. Effect of Solvents

The effect of the solvents is summarized in Table 5. In an alcohol, alkylbenzenes, ethers, and an alkane, the transfer hydrogenation proceeded well. This fact suggests that these solvents are not adsorbed on the catalyst so strongly as to act as poisons. As described previously, alcohols and ethers did not give hydrogen in this heterogeneous system. The incapacity of alcohols and ethers as hydrogen donors may be attributable, at least partly, to their low affinity to the catalyst. As the reduction of cycloheptene did not occur in ethanol in the absence of indoline, it is

TABLE 5
Effect of Solvents^a

Solvent	Yield of cycloheptane (%)
Ethanol	56
Ethanol ^b	0
Toluene	51
Anisole	45
Tetrahydrofuran	38
Diethyl ether	37
Dioxane	31
Decaline	30
Xylene	25
Methyl isobutyl ketone	11

^a Cycloheptene (0.25 *M*), indoline (0.50 *M*), and Pd/C (10 g/liter) were heated in the designated solvent at 90°C for 1 hr.

^b Indoline was not added.

confirmed that the alcohol used as a solvent gave no hydrogen to the olefin.

This reduction did not proceed at all in acetic acid, dimethyl sulfoxide, pyridine, aniline, chlorobenzene, *o*-dichlorobenzene, benzonitrile, nitrobenzene, and acetophenone. Perhaps the solvents in which the

TABLE 6
Effect of Additives^a

Additive	Yield of cycloheptane (%)
None	51
Indole	47
Sodium borohydride	42
Activated charcoal	35
Calcium oxide	28
Silica gel	24
Activated aluminum oxide	22
Pyridine	16
Stannous chloride	0
Chlorobenzene	0
Triphenylphosphine	0
Thiophene	0

^a Cycloheptene (0.25 *M*), indoline (0.50 *M*), Pd/C (10 g/liter) and the designated additive (10 g/liter) were heated in toluene at 90°C for 1 hr.

reduction did not occur behaved as poisons by covering the active sites of the catalyst.

5. Effect of Additives

It has been reported that the addition of carbon, alumina, silica, and tertiary amines activates palladium carbon (28). So the effect of several additives was investigated (Table 6). None of the additives including sodium borohydride promoted the hydrogenation. Some compounds which seem to be adsorbed strongly on the catalyst behaved as poisons.

6. Dependence on Reaction Time

To investigate the transfer hydrogenation in more detail, the dependence of the initial rate on several parameters was studied.

When indoline (0.50 *M*), cycloheptene (0.25 *M*), and Pd/C (10 g/liter) were heated at 90°C in toluene, the yield of cycloheptane was proportional to reaction time over the ranges up to 40% yield (Fig. 1). The linearity up to rather high conversion may be explained by the fact that the initial rate was not so varied in the region higher than 0.3 *M* in the indoline concentration and in the region of 0.2 ~ 0.6

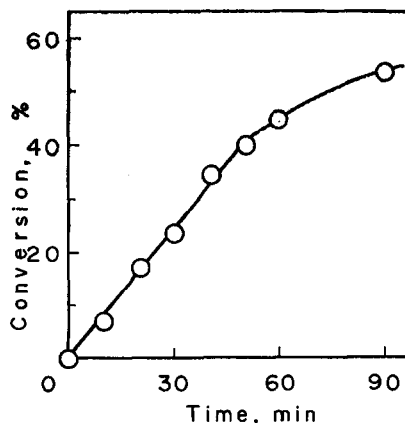


FIG. 1. The conversion of cycloheptene vs time curve. Indoline (0.50 *M*), cycloheptene (0.25 *M*), and Pd/C (10 g/liter) were heated in toluene at 90°C.

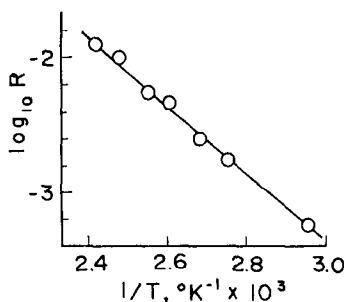


FIG. 2. Plot of $\log R$ vs $1/T$ ($^{\circ}\text{K}$). Indoline (0.50 M), cycloheptene (0.25 M), and Pd/C (10 g/liter) were heated in toluene.

M in the cycloheptene concentration, as described later. The initial rates of the reaction were derived from the linear parts in similar reactions.

7. Dependence on Temperature

Initial rates (R) were measured at the temperatures ranging $65 \sim 140^{\circ}\text{C}$ and a plot of $\log R$ against $1/T$ is shown in Fig. 2. A good linear plot is obtained, suggesting that this heterogeneous reaction is not diffusion-controlled (29). From Fig. 2, a value for the activation energy of $11.2 \text{ kcal mol}^{-1}$ and one for the activation enthalpy of $10.6 \text{ kcal mol}^{-1}$ were obtained. These values are smaller than the corresponding values in homogeneous transfer hydrogenation. For example, 21.4 (25), 21.6 (3), 31.4 (26), and $33.2 \text{ kcal mol}^{-1}$ (5) have been reported as the activation energies in the homogeneous systems.

8. Dependence on the Amount of the Catalyst

The reduction did not proceed when the amount of Pd/C was smaller than 2 g/liter (Fig. 3). Perhaps this fact may be explained by the inference that a definite amount of the catalyst is poisoned completely by a certain impurity, but the details of the poisoning are not clear as yet. When the amount of the catalyst was larger than 2 g/liter, a linear relation was observed between the initial rate and the amount of the catalyst.

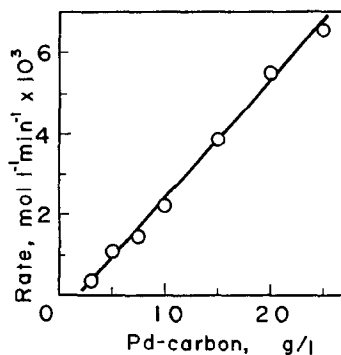


FIG. 3. Dependence of rate on the amount of Pd/C in toluene at 90°C with 0.50 M indoline and 0.25 M cycloheptene.

9. Dependence on the Indoline Concentration

When the concentration of indoline was lower than 0.3 M , the initial rate was proportional to the amine concentration (Fig. 4). However, in the region where the indoline concentration was higher than 0.3 M , the rate was independent of the donor concentration. This might mean that when the amine concentration was higher than 0.3 M , almost all the active sites of the catalyst were covered by indoline, hydrogen, and/or cycloheptene.

10. Dependence on the Cycloheptene Concentration

In the homogeneous transfer hydrogenations of cycloolefins, the reaction rates

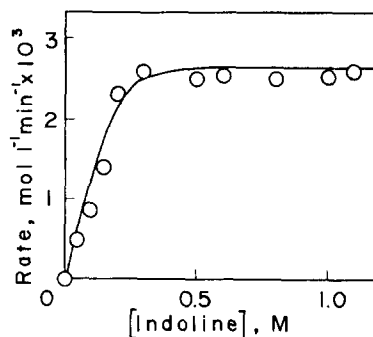


FIG. 4. Dependence of rate on the concentration of indoline. Indoline, cycloheptene (0.25 M), and Pd/C (10 g/liter) were heated in toluene at 90°C .

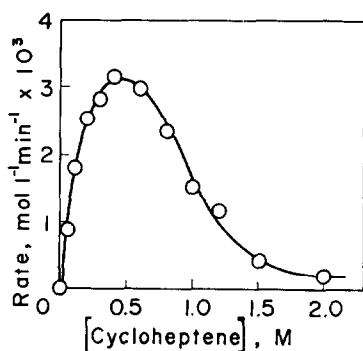
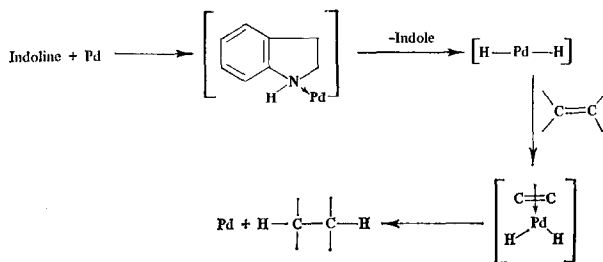


Fig. 5. Dependence of rate on the concentration of cycloheptene. Indoline (0.50 M), cycloheptene, and Pd/C (10 g/liter) were heated in toluene at 90°C.

were independent of the olefin concentrations and the dehydrogenation steps of hydrogen donors are inferred to be rate determining (3,5,25,26). It has been reported that in the reduction of cyclohexene and cyclooctene by molecular hydrogen catalyzed by Pd/C, the reaction rates are

almost independent of the olefin concentrations and the hydrogen transfer to the olefins is rate limiting (27). However, in this heterogeneous transfer hydrogenation, the initial rate showed a maximum at the cycloheptene concentration around 0.4 M (Fig. 5). This result shows that in higher concentration the olefin covered the active sites of the catalyst preferentially and retarded the adsorption of indoline and/or the dehydrogenation of indoline. In the cycloheptene concentration higher than 0.4 M, the adsorption of the olefin on the catalyst and the hydrogen transfer from the catalyst to the olefin could not be the rate-controlling step. Further, it is inferred that the adsorption power of cycloheptene is stronger than that of indoline, because the olefin poisoned the catalyst but the amine did not.

This transfer hydrogenation is speculated to proceed via following reaction path (22,30).



The rate-determining step of the heterogeneous transfer hydrogenation may be changed not only by the kind of hydrogen donors and hydrogen acceptors but also by the concentration of the donors and the acceptors.

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