References and Notes

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(20) Photolysis at 366 nm of this same reaction mixture yielded additional *cis*-stilbene with near unit quantum efficiency indicating that the products of the DBA–$TPPO_3$ reaction are not inhibitors of the stilbene sensitized isomerization. Hence the ^{3}NMA* counting experiment result is not in need of upward revision.
(21) From the other end of our error limits, we obtain $^1\Phi_{CE} = 0.018$ and Φ of ^{3}NMA* = 0.05 with the *maximum yield of directly formed* NMA* (excluding that from intersystem crossing) being $^3\Phi_{CE} = 0.04$. In view of the relatively large singlet–triplet splitting in NMA (probably $\gtrsim 10$ kcal/mol) we conclude that energetics are not dominating the competition between the chemiexcitation pathways directly leading to singlet and triplet NMA. The extent to which this result depends on the π,π^* nature of the low-lying excited states of NMA needs further elucidation.
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Transfer Hydrogenation and Transfer Hydrogenolysis. 11. Facile Dehydrogenation of Aromatic Hydrocarbons and the Mechanism of the Hydrogen Transfer from Indan, Tetralin, and Dioxane to Aldehydes Catalyzed by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

Hideaki Imai,* Takeshi Nishiguchi, and Kazuo Fukuzumi

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

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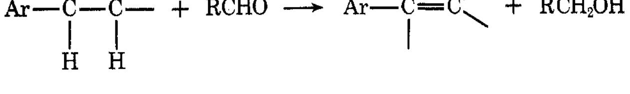
Aromatic hydrocarbons, such as indan and ethylbenzene, were dehydrogenated and reduced aldehydes under mild conditions in the presence of $RuH_2(PPh_3)_4$. It was also found that indan and isobutylbenzene reduced cycloheptene under more drastic condition in the presence of $RhCl(PPh_3)_3$. The mechanism of hydrogen transfer from indan, tetralin, and dioxane to an aldehyde catalyzed by $RuH_2(PPh_3)_4$ was investigated, and found to be different from that of the reduction of aldehydes by alcohols. The transfer hydrogenation by the aprotic substances occurs via dihydride complexes, and the overall rate law was rate = $a[DH_2][\text{cat.}]_0/(1 + b[DH_2] + c[RCHO])$ where $[DH_2]$, $[\text{cat.}]_0$, and [RCHO] are hydrogen donor, added catalyst, and aldehyde concentrations, respectively. The rate-determining step of the reduction by the aprotic hydrogen donors is the hydrogen transfer from the donors to the catalytic species.

In the catalytic transfer hydrogenation of carbonyl compounds, only primary and secondary alcohols[1] and formic acid[2] have been reported to donate hydrogen atoms under rather drastic conditions. We previously reported that ethers and hydroaromatic compounds also reduced aldehydes and ketones, and discussed the mechanism of the hydrogen transfer from alcohols to aldehydes catalyzed by $RuH_2(PPh_3)_4$.[3] Later, we found that aromatic hydrocarbons also gave hydrogen to aldehydes under mild conditions and to olefins under more drastic conditions. This study was undertaken to investigate the difference between the mechanism of the transfer hydrogenation of aldehydes by the protic hydrogen donors, alcohols, and that of the one by aprotic donors such as indan, tetralin, and dioxane.

Results and Discussion

Hydrogen-Donating Ability of Aromatic Hydrocarbons. Although the dehydrogenation of aromatic hydrocarbons has been carried out under drastic conditions in the presence of heterogeneous catalysts, we found that the dehydrogenation occurred under mild conditions with homogeneous catalysts. When an aromatic hydrocarbon (2.0 M), *n*-hexaldehyde (1.0 M), and $RuH_2(PPh_3)_4$ (0.02 M) were heated in bromobenzene at 36.5 °C, *n*-hexyl alcohol and a



$$\mathrm{Ar{-}\underset{H}{\overset{|}{C}}{-}\underset{H}{\overset{|}{C}}{-}} + \mathrm{RCHO} \longrightarrow \mathrm{Ar{-}\underset{|}{C}{=}C\!\!<} + \mathrm{RCH_2OH}$$

Table I. Transfer Hydrogenation of *n*-Hexaldehyde and Cycloheptene

		Yield of *n*-hexyl alcohol, %		
Registry no.	Hydrogen donor	I[a]	II[b]	Dehydrogenation product
25340-17-4	Diethylbenzene	12	24	*c*
496-11-7	Indan	13	22	Indene
25340-18-5	Triethylbenzene	11	21	*c*
104-51-8	*n*-Butylbenzene	10	20	*c*
538-93-2	Isobutylbenzene	10	20	1-Phenyl-2-methylpropene-1
1515-95-3	*p*-Ethylanisole	10	20	*c*
100-41-4	Ethylbenzene	9	18	Styrene
103-65-1	*n*-Propylbenzene	10	18	1-Phenylpropene-1
98-82-8	Isopropylbenzene	9	16	α-Methylstyrene
100-71-0	2-Ethylpyridine	11	15	*c*
6623-59-2	3,4-Dichloroethylbenzene	7	9	*c*
	Indan		28[d]	Indene
	Isobutylbenzene		9[d]	1-Phenyl-2-methylpropene-1

[a] $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor (2.0 M) were heated in bromobenzene at 36.5 ± 0.5 °C for 72 h. [b] $RuH_2(PPh_3)_4$ (0.02 M) and *n*-hexaldehyde (1.0 M) were heated in the designated hydrogen donor at 120 °C for 4 h. [c] Dehydrogenation product was not identified. [d] $RhCl(PPh_3)_3$ (0.02 M) and cycloheptene (0.5 M) were heated in the designated hydrogen donor at 180 °C for 6 h.

Table II. Transfer Hydrogenation of Carbonyl Compounds[a]

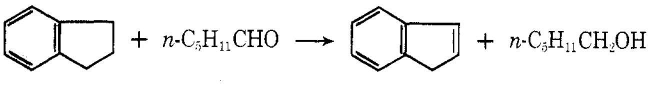
Registry no.	Substrate	Product	% yield
66-25-1	*n*-Hexaldehyde	*n*-Hexyl alcohol	22
110-62-3	*n*-Pentaldehyde	*n*-Pentyl alcohol	20
123-72-8	*n*-Butylaldehyde	*n*-Butyl alcohol	20
111-71-7	*n*-Heptaldehyde	*n*-Heptyl alcohol	16
123-38-6	Propionaldehyde	*n*-Propyl alcohol	16
124-13-0	*n*-Octaldehyde	*n*-Octyl alcohol	15
123-05-7	2-Ethyl-1-hexaldehyde	2-Ethyl-1-hexyl alcohol	14
78-93-3	Methyl ethyl ketone	2-Butyl alcohol	7
96-22-0	Diethyl ketone	3-Pentyl alcohol	7
67-64-1	Acetone	Isopropyl alcohol	6
100-52-7	Benzaldehyde	Benzyl alcohol	Trace

[a] $RuH_2(PPh_3)_4$ (0.02 M) and the substrate (1.0 M) were heated in indan at 120 °C for 4 h.

dehydrogenation product were obtained. However, the hydrogen transfer reaction was not catalyzed by $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $RhCl(PPh_3)_3$ even at 120 °C. As shown in Table I, all the aromatic hydrocarbons showed almost the same hydrogen-donating ability, and the yield of *n*-hexyl alcohol was quite low. This reaction is thought to be equilibrium limited, because the yield of *n*-hexyl alcohol was not improved by prolonged heating. This phenomenon is interpreted by the explanation that the alcohol produced is easily dehydrogenated to give the original aldehyde because the hydrogen-donating ability of the alcohol is superior to that of the aromatic hydrocarbons.

$$R^1CHO + R^2CH_2OH \rightarrow R^1CH_2OH + R^2CHO$$

When the reaction was carried out in the hydrogen donor at 120 °C, the yield of the alcohol somewhat increased. In substituted ethylbenzenes, the hydrogen-donating ability decreased in the order 4-ethylanisole > ethylbenzene > 3,4-dichloroethylbenzene. The hydrogen-donating ability is lowered by the electron-withdrawing substituents and this suggests the formation of cationic species in the transition state of the rate-determining step. Dehydrogenated donors were not quantitatively obtained except for indan. The complex $RuH_2(PPh_3)_4$ has been reported to catalyze the polymerization of olefinic compounds,[4] so the dehydrogenated alkylbenzenes are inferred to be lost by the polymerization. In the case of indan, the amount of the alcohol produced was equal to that of indene within experimental errors, and the following reaction is considered to proceed without significant side reactions.



The hydrogen transfer from indan and isobutylbenzene to cycloheptene also took place in the presence of $RhCl(PPh_3)_3$, but the reduction was hardly catalyzed by $RuH_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$.

Transfer Hydrogenation of Carbonyl Compounds. The reduction of several carbonyl compounds was examined in indan at 120 °C (Table II), and aliphatic aldehydes were found to be reduced most easily. The yield of the alcohols was not varied so much with the structure of the aliphatic aldehydes, but the aldehydes having moderate steric hindrance were inclined to give the corresponding alcohols in higher yield. The steric effect is explained by these assumptions: (1) As shown later (Scheme II), the coordination of two aldehyde molecules may inhibit the transfer hydrogenation, and the most appropriate coordinating power of the aldehydes exists. (2) As described earlier, this reaction is equilibrium limited, and the alcohol formed competes with the other hydrogen donor for a coordination site of the catalyst. Therefore, in the balance of the coordinating power between the aldehydes and the corresponding alcohols which is affected by the alkyl residues of the aldehydes, the most favorable steric hindrance of the aldehyde exists. Aliphatic ketones were more difficultly re-

Table III. Solvent Effect[a]

Solvent	Rate, mol l.$^{-1}$ min^{-1} × 10^3	Solvent	Rate, mol l.$^{-1}$ min^{-1} × 10^3
Benzene	1.8	Chlorobenzene	1.4
p-Xylene	1.8	Diethyl ether	1.4
o-Dichlorobenzene	1.8	Methyl benzoate	1.3
n-Hexane	1.7	Acetonitrile	1.1
Bromobenzene	1.4	Dimethyl sulfoxide	1.1
Anisole	1.4		

[a] $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and indan (2.0 M) were heated at 80 °C.

duced, perhaps because the secondary alcohols formed are more effective as hydrogen donors than the primary alcohols. Benzaldehyde and acetophenone were hardly reduced, and this fact is interpreted by the explanation that the carbonyl group is stabilized by the resonance with the benzene ring and the hydrogen donating ability of benzylic alcohols is stronger than that of the other aliphatic alcohols. *N,N*-Dimethylacetamide and ethyl acetate were not reduced.

Unless otherwise noted, *n*-hexaldehyde was used as a hydrogen acceptor in all the experiments in this study, because of the ease in GC analysis.

Reaction Solvent. Although the transfer hydrogenation of olefins hardly proceeded in polar solvent such as chlorobenzene,[5,6] the rate of the reduction of *n*-hexaldehyde by indan was not influenced so much by solvents (Table III). This observation shows that the coordination of the aldehyde is stronger than that of olefins and so strong as not to be affected by solvents. The strong coordination ability of aldehydes has been shown by spectroscopic study[3] and by the effect of addition of triphenylphosphine and olefins. In spite of the low solubility of the catalyst in *n*-hexane and ether at room temperature, it immediately dissolved to give a red-brown solution in the presence of the aldehyde. This also shows that the aldehyde coordinates so strongly as to form a complex rapidly with the catalyst. In the other experiments in this study, bromobenzene was used as a solvent.

Measurement of Initial Rate. We have previously reported that the hydrogen transfer from tetralin and dioxane to *n*-hexaldehyde catalyzed by $RuH_2(PPh_3)_4$ occurred without side reactions.[3] Then the kinetic study of the reduction of the aldehyde, in which indan, tetralin, and dioxane were used, was carried out to investigate the reaction mechanism and to compare it with the mechanism of the reduction by alcohols. The yield of the alcohol was proportional to the reaction time up to several percent as shown in Figure 1 and the initial rate of the reduction (R) was derived from the linear part. The linear part was narrower than that of other transfer hydrogenations and it is inferred to be caused by the dehydrogenation of the produced alcohol.

The initial rate of the reduction was proportional to the catalyst concentration (Figure 2), and the plot of the reciprocal of the rate against the reciprocal of the concentration of the hydrogen donors was linear with a positive intercept on the y axis (Figure 3). In the reduction of the aldehyde by alcohols, the rate was in proportion to the concentration of the alcohol.[3] The difference in the dependence of the rate on the hydrogen donor concentration may be due to the difference in the reaction mechanisms. The initial rate of the reduction decreased with the increase of the aldehyde concentration. The plot of the reciprocal of the rate against the aldehyde concentration was linear with a positive intercept on the y axis, as shown in Figure 4. This agrees with the result obtained in the reduction by alcohols.[3]

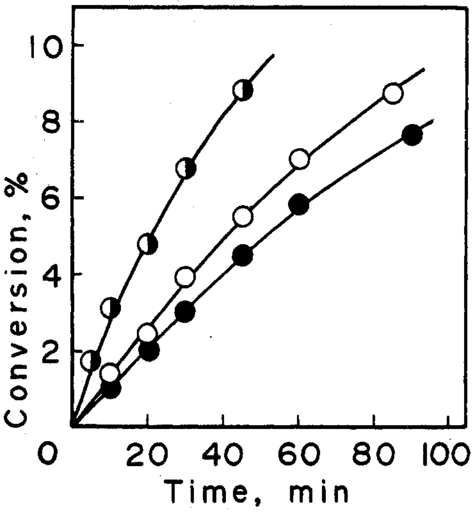


Figure 1. Plots of conversion vs. reaction time: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor were heated in bromobenzene at 80 °C; (○) indan, (●) dioxane (2.0 M), and (◑) tetralin (1.0 M).

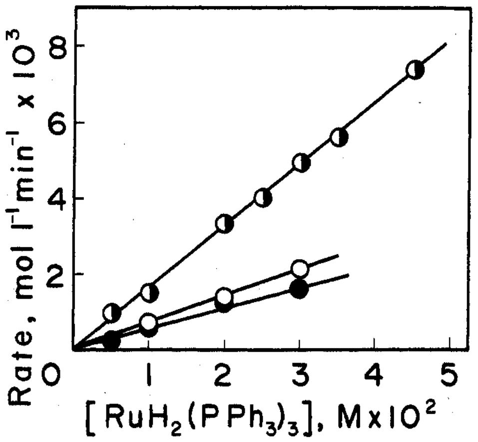


Figure 2. Dependence of the rate of the reduction of *n*-hexaldehyde on catalyst concentration: the catalyst, *n*-hexaldehyde (1.0 M), and the hydrogen donor were heated in bromobenzene at 80 °C; (○) indan, (●) dioxane (2.0 M), and (◑) tetralin (1.0 M).

Reaction Temperature. Initial rates were measured at several temperatures ranging from 60 to 110 °C, and the plots of log R against $1/T$ show a good linear relationship. From the plots, activation energy, E_a, and activation enthalpy, $\Delta H^{\ddagger}$, were obtained, and activation entropy, $\Delta S^{\ddagger}$, was derived from the rate constant, k_4, which will be defined later. The values of the corresponding parameters were nearly equal mutually in the reduction of the aldehyde by indan, dioxane, and tetralin (Table IV). This suggests the similarity in the reaction mechanism. The activation energy and the activation enthalpy of the reduction by isopropyl alcohol are higher than those of the corresponding reduction by the aprotic hydrogen donors. Further, the values of the three parameters of the reductions of the aldehyde by the protic and the aprotic hydrogen donors are greatly lower than those of the corresponding parameters

Table IV. Kinetic Parameters

Registry no.	Hydrogen donor	Hydrogen acceptor	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
	Indan	*n*-Hexaldehyde	7.4	6.7	−44.3
119-64-2	Tetralin	*n*-Hexaldehyde	6.8	6.1	−43.3
123-91-1	Dioxane	*n*-Hexaldehyde	6.8	6.1	−46.3
67-63-0	Isopropyl alcohol	*n*-Hexaldehyde	11.0	10.3	−42.5
	Isopropyl alcohol	Cyclohexene	31.4	30.7	20

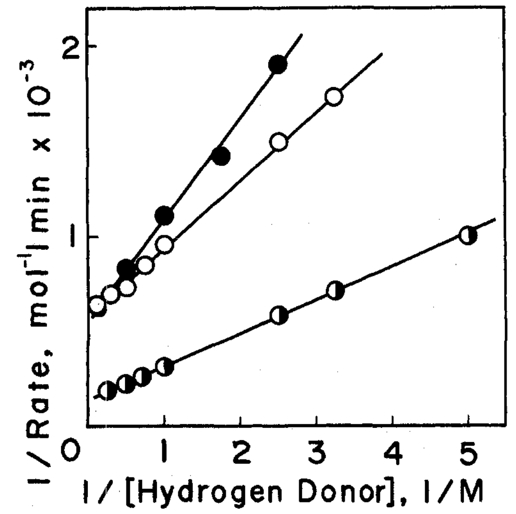


Figure 3. Dependence of the rate of the reduction of *n*-hexaldehyde on the hydrogen donor concentration: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor were heated in bromobenzene at 80 °C; (○) indan, (●) dioxane, and (◑) tetralin.

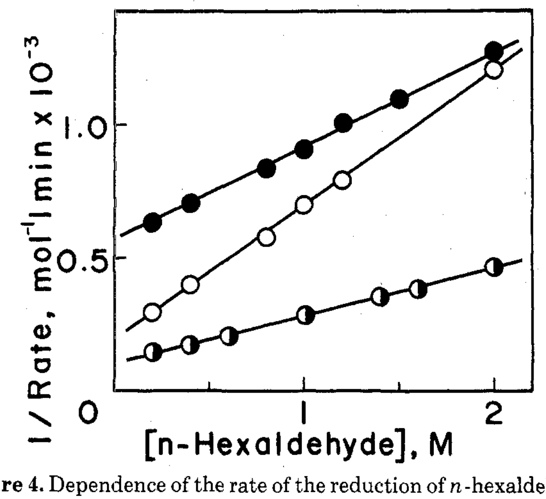


Figure 4. Dependence of the rate of the reduction of *n*-hexaldehyde on the aldehyde concentration: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde, and the hydrogen donor were heated in bromobenzene at 80 °C; (○) indan, (●) dioxane (2.0 M), and (◑) tetralin (1.0 M).

of the reduction of cyclohexene by the alcohol. The small value of the activation entropy indicates that the transition states of the reductions of the aldehydes are more crowded or more ordered than that of the hydrogenation of olefins.[7] Therefore, the reaction mechanism for the reduction of aldehydes by the protic and the aprotic compound considerably differed from that of olefins by alcohols.

Kinetic Isotope Effect. The initial rate was 1.1×10^{-3} mol l.$^{-1}$ min^{-1} in the reaction in which *n*-hexaldehyde (1.0 M), dioxane (1.0 M), and the catalyst (0.2 M) were heated in bromobenzene at 80 °C, while it was 5.5×10^{-4} mol l.$^{-1}$ min^{-1} in the reduction in which octadeuteriodioxane was used instead of dioxane. The value of the kinetic isotope effect, $R_H/R_D = 2.0$, shows that a hydrogen transfer step is rate limiting. In this reaction, the hydrogen transfer occurs twice. One is the transfer from the hydrogen donor to the central metal of the catalyst and the other is that from the dihydride complex to the coordinated aldehyde. The former is inferred to be rate limiting, because the reaction between *n*-hexaldehyde and $RuH_2(PPh_3)_4$ completed within 1 min at 80 °C and quantitatively gave *n*-hexyl alcohol as a product. Unlike this result, the value of the kinetic isotope effect was 0.9 in the reduction of the aldehyde by isopropyl alcohol, and the coordination of the alcohol is concluded to be the rate-determining step.[3] Based on the fast hydrogen transfer from $RuH_2(PPh_3)_4$ to the aldehyde, the first step of the catalytic cycle is considered to be the transfer of the hydride ligands of the complex to aldehyde, as reported previously.[3,6]

Scheme I

$$RuH_2(PPh_3)_4 + RCHO \rightarrow RuH_2(PPh_3)_3(RCHO) + PPh_3$$

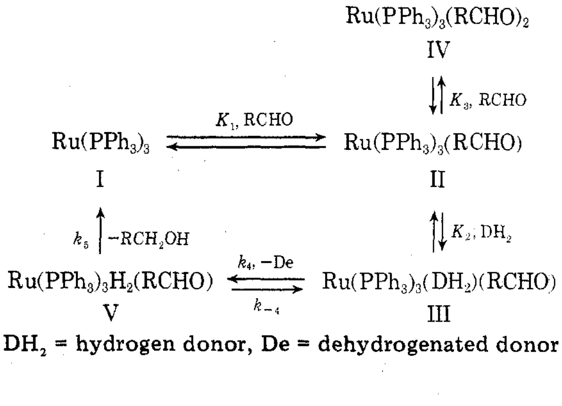
$$RuH_2(PPh_3)_3(RCHO) \xrightarrow{S} Ru(PPh_3)_3 + RCH_2OH$$

S = solvent

Effect of Additives. To investigate the reaction process, the effect of additives was examined at 80 °C. Although the rate of the transfer hydrogenations of olefins was lowered by the addition of triphenylphosphine in almost all cases,[5,6,8] that of the reduction of the aldehydes by the aprotic hydrogen donors was not changed at all by the addition of the phosphine over concentration range of 0.01–0.1 M. This fact shows that the release of the phosphine from the catalyst occurs easily. The rate of the reduction of the aldehyde was not decreased by the addition of indene, dioxene, cyclohexene, and hexene-1, and neither the hydrogenation of cyclohexene and hexene-1 nor the isomerization of hexene-1 was observed. This fact suggests that the coordinating ability of the aldehyde is far larger than that of the olefins and the dehydrogenated donors, and perhaps larger than that of hydrogen donors which seems to be comparable to that of the dehydrogenated donors. The addition of ethyl alcohol increased the rate of the reduction of the aldehyde, because the alcohol acts as a hydrogen donor. This observation is consistent with the early deviation from the linear dependence of the conversion of the aldehyde against reaction time, as described before.

Kinetic Discussion. The studies of the hydrogen transfer from isopropyl alcohol to olefins[6] and aldehydes[3] by $RuH_2(PPh_3)_4$ have been already reported. Based on those studies and the results described in the previous section, we should like to propose the following catalytic cycle for the

Scheme II



DH_2 = hydrogen donor, De = dehydrogenated donor reaction scheme of the reduction of the aldehyde by the aprotic hydrogen donors. The first step of this transfer hydrogenation is presumed to be the formation of $Ru(PPh_3)_3$ or its solvated species, as described earlier.

It is assumed that the intermediate, V, is sufficiently reactive and scarce for steady-state treatment to be applied, because the reaction between $RuH_2(PPh_3)_4$ and *n*-hexaldehyde occurred very fast. From the assumption and Scheme II, the rate is expressed as

$$R = \frac{k_4k_5K_1K_2[\mathrm{RCHO}][\mathrm{DH_2}][\mathrm{cat.}]_0}{(k_{-4}[\mathrm{De}] + k_5)[1 + K_1[\mathrm{RCHO}](1 + K_3[\mathrm{RCHO}] + K_2[\mathrm{DH_2}])]} \tag{1}$$

where K_1, K_2 and K_3 are equilibrium constants, k_4 and k_5 are rate constants, and $[\mathrm{DH_2}]$, [RCHO], [De], and $[\mathrm{cat.}]_0$ are the concentration of the hydrogen donors, the aldehyde, the dehydrogenated donors, and the added catalyst, respectively. As the dehydrogenated donors were not reduced, the term of $k_{-4}[\mathrm{De}]$ is negligible. Then eq 1 is reduced to

$$R = \frac{k_4K_1K_2[\mathrm{RCHO}][\mathrm{DH_2}][\mathrm{cat.}]_0}{1 + K_1[\mathrm{RCHO}](1 + K_3[\mathrm{RCHO}] + K_2[\mathrm{DH_2}])} \tag{2}$$

As the reciprocal of the rate depended linearly on the aldehyde concentration, the following relation should be satisfied in the denominator of eq 2: $1 \ll K_1[\mathrm{RCHO}](1 + K_3[\mathrm{RCHO}] + K_2[\mathrm{DH_2}])$, that is, $\mathrm{I} \ll \mathrm{II} + \mathrm{III} + \mathrm{IV}$. This relation is consistent with the fact that the coordination power of the aldehyde is strong. Therefore, eq 3 becomes

$$R = \frac{k_4K_2[\mathrm{DH_2}]}{1 + K_2[\mathrm{DH_2}] + K_3[\mathrm{RCHO}]}[\mathrm{cat.}]_0 \tag{3}$$

This expression accommodates all the experimental results. As an example of the analysis of eq 3, the reduction by dioxane is described. (a) The rate shows the first-order dependence on the catalyst concentration in both Figure 1 and eq 3, and the value of 0.028 min^{-1} was obtained as the value of the coefficient of the catalyst concentration in eq 3 from the gradient of the plot of Figure 1. (b) Equation 3 is rearranged as follows:

$$1/R = \frac{1}{k_4[\mathrm{cat.}]_0} + \frac{1 + K_3[\mathrm{RCHO}]}{k_4K_2[\mathrm{cat.}]_0}\,\frac{1}{[\mathrm{DH_2}]} \tag{4}$$

This equation is consistent with the plot of Figure 2, and the value of the intercept, 580 mol^{-1} l. min, and the one for the gradient, 600 min, were obtained as the value of the first term and the coefficient of the second term, respectively. (c) Equation 3 can be rearranged as follows:

$$1/R = \frac{1 + K_2[\mathrm{DH_2}]}{k_4K_2[\mathrm{DH_2}][\mathrm{cat.}]_0} + \frac{K_3}{k_4K_2[\mathrm{DH_2}][\mathrm{cat.}]_0}[\mathrm{RCHO}] \tag{5}$$

From Figure 3, the value for the intercept, 600 mol $\mathrm{l.}^{-1}$ min, and the one for the gradient, 280 mol^{-2} $\mathrm{l.}^2$ min, were obtained as the value of the first term and the coefficient of the second term of eq 5, respectively. From these values, 6.3 mol^{-1} l., 6.4 mol^{-1} l., and 0.09 min^{-1} were obtained as the values of K_2, K_3, and k_4. Therefore, in the reduction of *n*-hexaldehyde by dioxane in bromobenzene at 80 °C, the overall rate is expressed as follows:

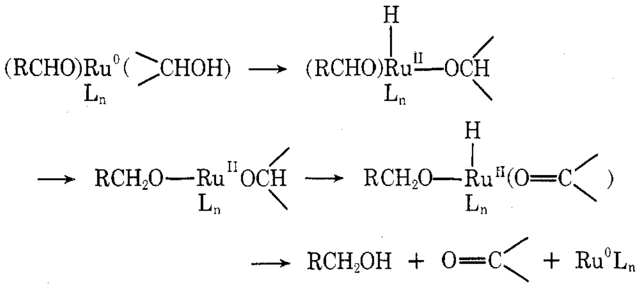
$$R = \frac{0.57[\mathrm{DH_2}][\mathrm{cat.}]_0}{1 + 6.3[\mathrm{DH_2}] + 6.4[\mathrm{RCHO}]} \tag{6}$$

Table V. Kinetic and Equilibrium Constants

Hydrogen donor	k_4, min^{-1}	K_2, mol $\mathrm{l.}^{-1}$	K_3, mol $\mathrm{l.}^{-1}$	K_2/K_3
Indan	0.11	5.0	5.5	0.91
Tetralin	0.42	3.8	4.2	0.90
Dioxane	0.09	6.3	6.4	0.98

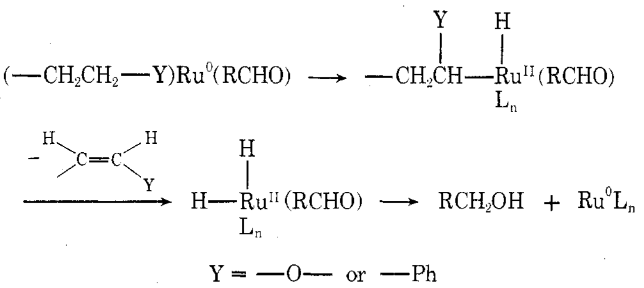
The values of K_2, K_3, and k_4 are summarized in Table V. The relative values of the coordinating power of the hydrogen donors may be estimated by the values of K_2/K_3 ratio, and that of dioxane was found to be a little larger than that of indan and tetralin. This may be due to the difference of the way of the coordination, that is, dioxane coordinates on the catalyst with the oxygen, while indan and tetralin do with their benzene rings. The value of k_4 in the reaction of tetralin was about four times larger than that in the reaction of indan or dioxane. This fact might be explained by the relative stability of the intermediates derived from the donors.[9] The similarity of all the kinetic behaviors and constants except for k_4 indicates that the hydrogen transfer from indan, tetralin, and dioxane to aldehydes occurs in a similar way. However, the mechanism of this reduction is different from that of the reduction of aldehydes by alcohols. As described before, the outcome of the kinetic isotope effect varied one from another. Moreover, the rate was proportional to the donor concentration in the reduction by alcohols, but such a relation was not observed in the reduction by the aprotic hydrogen donors. According to the hydrogen transfer from alcohols to aldehydes, we previously proposed such a mechanism as shown in Scheme III, which involves the oxidative addition of O–H bond to a Ru^0 species.[3] The coordination of alcohols is concluded to be the rate-determining step.

Scheme III



This mechanism cannot be applied to the reduction by the aprotic donors. Therefore, we should like to propose the following mechanism in which the oxidative addition of a C–H bond is the rate-determining step.

Scheme IV



The mechanism of the reduction of aldehydes by the protic and aprotic hydrogen donors is different from that of the reduction of olefins by alcohols. This is supported by the fact that aldehydes coordinated rapidly on ruthenium species but olefins hardly did, and that in the reduction of olefins by alcohols ruthenium species exist mainly in the form of $Ru(PPh_3)_3$ or its solvated form,[6] while in the reduction of aldehydes by alcohols a ruthenium–aldehyde complex was obtained.[3] The transfer hydrogenation of aldehydes occurred at lower temperatures than that of olefins.[3] This fact suggests that the catalyst was activated by the coordination of one aldehyde molecule, because the dehydrogenation from the donors is rate limiting both in the reduction of olefins by alcohols and in that of aldehydes by the aprotic donors. Anyway, the relative strength of the coordinating power of hydrogen donors and hydrogen acceptors is one of the important factors to control the reaction mechanisms of transfer hydrogenations.

In the reduction at 80 °C in bromobenzene, tetralin, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene reduced *n*-hexaldehyde at the initial rate of 3.2, 8.5, and 2.5 × 10^{-3} mol $1.^{-1}$ $\min^{-1}$, respectively. 1,4-Dihydronaphthalene showed the lowest reduction rate, and the rate of the isomerization to 1,2-dihydronaphthalene was far higher than that of the reduction of the aldehyde. We formerly considered that the driving force of the hydrogen transfer from tetralin was the increase of the aromatization energy caused by the formation of naphthalene. However, the dehydrogenation rate of dihydronaphthalenes was not so much higher than that of tetralin. Moreover, it was found that the main product in the earlier stage of the reduction of aldehydes by tetralin was not naphthalene but 1,2-dihydronaphthalene. These results show that the driving force of the hydrogen-donating ability of tetralin was not derived from the stabilization by the aromatization. We now consider that the hydrogen donating abilities of the aprotic donors examined were affected by the stabilities of the cationic intermediates.

Experimental Section

All the transfer hydrogenations and kinetic measurements were carried out by the method reported previously.[3,5,6,8,10]

Materials. Chlorotris(triphenylphosphine)rhodium(I),[12] dichlorotris(triphenylphosphine)ruthenium(II),[13] hydridotetrakis(triphenylphosphine)rhodium(I),[14] and dihydridotetrakis(triphenylphosphine)ruthenium(II)[14] were prepared by methods reported in the literature. Aldehydes were purified by distillation followed by dehydration with molecular sieves. Tetralin, indan, 1,2-dihydronaphthalene, and dioxane were purified by distillation and dried by usual methods. All solvents were purified by distillation. 1,4-Dihydronaphthalene and 3,4-dichloroethylbenzene were synthesized by methods of Cook[15] and Marvel,[16] respectively.

Registry No.—Cycloheptene, 628-92-2; hexyl alcohol, 111-27-3; dihydridotetrakis(triphenylphosphine)ruthenium(II), 19529-00-1.

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(9) The hydrogen donor seems to be cationic in the transition state of the dehydrogenation catalyzed by transition metal complexes.[1h,10,11] This inference is supported by the substituent effect of ethylbenzenes which was described earlier. The cationic intermediate derived from tetralin seems to have higher stability than the one from indan. This reasoning is based on the inference that the nine carbon atoms of them have a tendency to lie in a plane by the benzyl type resonance (this means that all the carbon atoms of the intermediate derived from indan endeavor to lie in a plane).

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A Survey of Structural Effects on Formation Constants in C–H Hydrogen Bonding[1]

Floyd M. Slasinski, James M. Tustin, Francis J. Sweeney, Alan M. Armstrong, Quazi A. Ahmed, and John P. Lorand*

Filson Chemistry Laboratories, Central Michigan University, Mount Pleasant, Michigan 48859

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Formation constants, K, for the association of a variety of C–H donors with HMPA have been measured by application of Higuchi's iterative method to ^{1}H NMR data for CCl_4 solutions at 35 °C. Infrared shifts have been measured using Me_2SO-d_6 in CCl_4 or $CDCl_3$. The donors include sp^3, sp^2, and sp systems. As previously reported, K's correlate so poorly with ir shifts that the latter have no predictive value as to the strength of H-bond complex formation for C–H donors. The largest K's are found in sp^3 systems because of the possibility of three electronegative α substituents. K's for terminal acetylenes are more sensitive to their single β substituent, covering a range of at least 100-fold. K's are reported for the first time for vinyl and aromatic C–H bonds; those for the latter are small. Substituents affect K values for sp^3 systems in the order $CN \simeq NO_2 > SCN$, p-O_2N-$C_6H_4 > F, Cl, Br > CONMe_2 > CO_2R \geq C_6H_5$, which differs markedly from that observed for Bronsted proton transfer in solution. Similar orders are followed in the sp^2 and sp series. Substituent effects are only crudely correlated by Taft σ_I constants. It is suggested that substituent effects in C–H hydrogen bonding reflect a greater contribution from the through-bond inductive effect than in other systems.

The participation of C–H bonds in hydrogen bonding has long been recognized, as for chloroform and terminal acetylenes.[2] Their hydrogen bonds with strong acceptors, such as pyridine and Me_2SO, as well as with weaker ones such as acetone, are readily detected by ir and ^{1}H NMR spectral shifts. A detailed survey of ir shifts by Allerhand and Schleyer,[3] utilizing fully deuterated Me_2SO and pyridine, has shown clearly that certain vinyl and aromatic C–H bonds also undergo hydrogen bonding, and that shifts for saturated systems are enhanced much more by an α-cyano group than by α-