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KINETICS AND MECHANISM OF THE TRANSFER HYDROGENATION AND DOUBLE BOND MIGRATION OF 1-HEXENE CATALYZED BY MOLYBDENUM COMPLEXES

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Summary

The mechanism of the transfer hydrogenation and double bond migration of 1-hexene catalyzed by *trans*-$Mo(N_2)_2(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$) has been studied. The stoichiometric reaction of 1-hexene with $MoH_4(dpe)_2$ suggests that the active species for the hydrogenation is $MoH_2(dpe)_2$ and that for the double bond migration it is $Mo(dpe)_2$. The double bond migration is suppressed in the hydrogenation of 1-hexene by molecular hydrogen, with the formation of a moderate amount of hexane. The result of the reaction of $Mo(C_2H_4)_2(dpe)_2$ with 2-propanol suggests that dual pathways may be available for the transfer hydrogenation. The kinetics of the hydrogen transfer from 2-propanol to 1-hexene, however, indicate that the predominant pathway involves the reaction of the catalyst with 2-propanol, giving the hydride, followed by 1-hexene coordination. The double bond migration which occurs in the presence of 2-propanol is inferred to proceed by a σ-alkyl mechanism which is different from that in the absence of 2-propanol.

Introduction

There is considerable interest in catalyzed homogeneous transfer hydrogenations of ketones and olefins using donor solvents such as alcohols and hydroaromatic compounds [1]. Group VIII metal complexes are widely used, and mechanistic studies have been reported for these complexes. The mechanisms of transfer hydrogenation are roughly divided into two groups. The first mechanism, exemplified by alcohol as donor, invokes coordination of the acceptor, then coordination of the alcohol and formation of a metal alkoxide, followed by β-hydrogen transfer from the alkoxide and release of product [2, 3]. This mechanism is similar to an 'unsaturate' route in the reduction using molecular hydrogen [4]. The second mechanism involves prior coordination of the donor followed by that of the acceptor, similar to a 'hydride' route [2]. Formation of an intermediate dihydride from a donor

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has also been invoked [5]; in mechanistic terms, the hydrogenation then becomes equivalent to the reaction using molecular hydrogen.

Recently we have reported the first example of Group VI metal catalysts for transfer hydrogenation; *trans*-$Mo(N_2)_2(dpe)_2$ and $MoH_4(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$) are active in the transfer hydrogenation of ketones [6, 7] and olefins [7] by secondary alcohols. The transfer hydrogenation of α-olefins is accompanied by double bond migration. In this paper we report the results of a study to elucidate the mechanism of the transfer hydrogenation and double bond migration of 1-hexene catalyzed by *trans*-$Mo(N_2)_2(dpe)_2$.

Experimental

All reactions were carried out under prepurified Ar unless otherwise noted. 1-Hexene and pyrrolidine were dried over sodium, 2-propanol was dried over calcium oxide and cyclohexanone was dried with Drierite ($CaSO_4$). These reagents were distilled before use under Ar. Solvents were dried and distilled under Ar using standard techniques. $MoH_4(dpe)_2$ [8], *trans*-$Mo(N_2)_2(dpe)_2$ [9], $Mo(C_2H_4)_2(dpe)_2$ [10], and *trans*-$W(N_2)_2(dpe)_2$ [11] were prepared by literature methods. Infrared spectra were obtained on a Nihon Bunko IRA-2 spectrometer.

Reaction of 1-hexene with $MoH_4(dpe)_2$

A solution of $MoH_4(dpe)_2$ (90 mg, 0.10 mmol) in toluene (4 ml) was heated in a 40-ml three-necked Schlenk-type flask at 80 °C. Samples of the reaction gas were withdrawn by syringe through a serum cap and analyzed by GLC on a molecular sieve 5A column. Evolution of H_2 (0.090 mmol) was confirmed. Into the solution 1-hexene (42 mg, 0.50 mmol) was added by syringe through the serum cap at $t = 0$ and the total volume of the solution was made up to 5.0 ml. GLC analysis of the liquid phase was performed on a Durapak octane/Porasil C column using benzene as an internal standard.

The reaction of 1-hexene with *trans*-$Mo(N_2)_2(dpe)_2$ was carried out in a similar manner.

Reaction of $Mo(C_2H_4)_2(dpe)_2$ with 2-propanol

A solution of $Mo(C_2H_4)_2(dpe)_2$ (95 mg, 0.10 mmol) in benzene (4 ml) was heated in a 40-ml three-necked Schlenk-type flask at 80 °C. GLC analysis of the gas phase on a Porapak Q column showed formation of C_2H_4 (0.10 mmol) and C_2H_6 (0.004 mmol). Into the solution 2-propanol (180 mg, 3 mmol) was added at $t = 0$ and the total volume made up to 5.0 ml.

Reaction of $Mo(C_2H_4)_2(dpe)_2$ with other donors was carried out in a similar manner.

Reaction of trans-$W(N_2)_2(dpe)_2$ with 2-propanol

A mixture of *trans*-$W(N_2)_2(dpe)_2$ (104 mg, 0.10 mmol) and 2-propanol (180 mg, 3 mmol) in toluene (4 ml) was heated at 80 °C for 2 h. GLC analysis of the gas phase on a molecular sieve 5A column showed formation of H_2 (0.0065 mmol). GLC analysis of the liquid phase on a 10% PEG 20M/ Chromosorb W column indicated formation of acetone (0.11 mmol). Addition of hexane (6 ml) deposited yellow crystals of $WH_4(dpe)_2$ [12], which were filtered, washed with hexane, and dried *in vacuo* (73 mg, 74% yield): IR (KBr) ν(W—H) 1785, 1845 cm^{-1}. Anal. ($C_{52}H_{52}WP_4$), C, H.

Kinetic experiments

All kinetic runs were carried out in dry, degassed solvent and were followed by monitoring the concentrations of hydrocarbons with GLC. The concentration of *trans*-$Mo(N_2)_2(dpe)_2$ in solution was above 0.0065 M. When the catalyst concentration was lower than 0.0065 M, the activity was lower than expected and often essentially zero, which may be due to the unavoidable presence of oxygen.

Results and discussion

Reaction of 1-hexene with $MoH_4(dpe)_2$ or trans-$Mo(N_2)_2(dpe)_2$

In the absence of acceptors, *trans*-$Mo(N_2)_2(dpe)_2$ reacted with secondary alcohols or hydroaromatic compounds to yield dehydrogenation products and $MoH_4(dpe)_2$ [13], which also has proved to be a catalyst for transfer hydrogenation [6, 7].* Furthermore, $MoH_4(dpe)_2$ was obtained from the solution in which hydrogen transfer from secondary alcohols to olefins in the presence of *trans*-$Mo(N_2)_2(dpe)_2$ was carried out. Thus the stoichiometric reaction between $MoH_4(dpe)_2$ and olefins seems of interest, although $MoH_4(dpe)_2$ itself would not be expected to interact with olefins, as it is coordinatively saturated.

Figure 1 shows the behavior of 1-hexene toward $MoH_4(dpe)_2$ in the absence of a donor. At 80 °C in toluene under Ar prior to addition of 1-hexene, $MoH_4(dpe)_2$ released 0.90 molar equiv of H_2, which was confirmed by GLC. On cooling the resulting solution, $MoH_4(dpe)_2$ was recovered quantitatively. From these observations we presumed that reversible elimination of molecular hydrogen from $MoH_4(dpe)_2$ occurred**, and that MoH_2-$(dpe)_2$ is the predominant species at 80 °C in toluene (eqn. (1)). When 1-hexene (1-hexene/Mo = 5) was injected, the rapid formation of hexane was observed.

$$MoH_4(dpe)_2 \underset{H_2}{\overset{-H_2}{\rightleftarrows}} MoH_2(dpe)_2 \qquad (1)$$

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*Hydrogenation with molybdenum hydrides formed in the reaction of Mo atoms with tetrahydrofuran has very recently been reported [14].

**A dissociative reaction of this type has been inferred recently in the water–gas shift reaction on $Mo(CO)_6$ [15], and is generally believed to be assisted by incoming carbon monoxide.

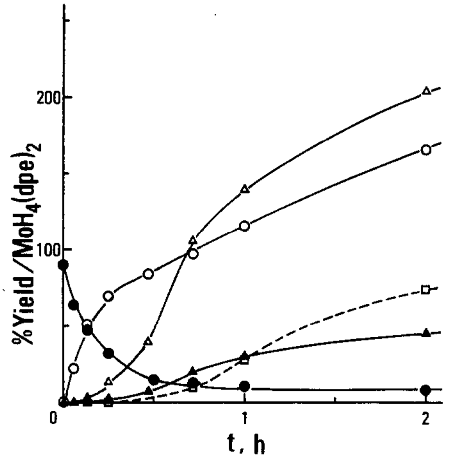


Fig. 1. Time course of the reaction of 1-hexene with $MoH_4(dpe)_2$ in toluene at 80 ± 0.1 °C. $[MoH_4(dpe)_2] = 2.0 \times 10^{-2}$ M; $[\text{1-hexene}] = 1.0 \times 10^{-1}$ M; ○, hexane; △, *trans*-2-hexene; ▲, *cis*-2-hexene; ●, H_2; □, $Mo(dpe)_2$ calculated.

The amount of gas-phase H_2 simultaneously decreased, which suggests that H_2 again coordinated to molybdenum. It is notable that there was an induction period in the formation of *cis*- and *trans*-2-hexene; the double bond migration did not proceed until the gas-phase H_2 concentration fell off. Consequently, when an amount of 1-hexene equivalent to that of $MoH_4(dpe)_2$ was added (1-hexene/Mo = 2), most of the 1-hexene was converted to hexane and only 11% (based on $MoH_4(dpe)_2$) of 2-hexenes were formed. In the presence of a large excess of 1-hexene, 2-hexenes were catalytically formed, during which time a quantitative yield of hexane was obtained (Table 1).

Attempts to obtain NMR evidence for $MoH_2(dpe)_2$ were unsuccessful; therefore it is difficult to rule out the possibility of the presence of $MoH_3(dpe)(C_6H_4PhPCH_2CH_2PPh_2)$, which should be formed by oxidative addition of the *ortho* C—H bond of dpe. However, the apparent 18-electron 8-coordinate complex $MoH_3(dpe)(C_6H_4PhPCH_2CH_2PPh_2)$ is coordinatively saturated, and would not be expected to interact with olefins. Thus it is tempting to speculate that the apparent 16-electron $MoH_2(dpe)_2$ complex itself reacts with 1-hexene to give hexane, although the complex might be in equilibrium with the $MoH_3(dpe)(C_6H_4PhPCH_2CH_2PPh_2)$ species.

Table 1 shows the behavior of *trans*-$Mo(N_2)_2(dpe)_2$ toward 1-hexene. Unlike $MoH_4(dpe)_2$, *trans*-$Mo(N_2)_2(dpe)_2$ showed no induction period in the double bond migration of 1-hexene (Fig. 2). When heated at 80 °C in toluene under Ar prior to addition of 1-hexene, *trans*-$Mo(N_2)_2(dpe)_2$ released 1.7 molar equiv of N_2, suggesting the formation of a significant amount of a doubly coordinatively unsaturated species, $Mo(dpe)_2$ (eqn. (2)). The five-coordinate species $Mo(N_2)(dpe)_2$ was presumed to be an intermediate in the substitution and alkylation reactions of *trans*-$Mo(N_2)_2(dpe)_2$ [16], and is isoelectronic with the stable carbonyl complex $Mo(CO)(dpe)_2$ [17]. The postulated species $Mo(dpe)_2$ is closely related to $W(dpe)_2$ which was

TABLE 1

The reaction of 1-hexene catalyzed by molybdenum complexes[a]

Catalyst	Atmosphere	Donor	Yield (%)[b]	
			Hexane	2-Hexene
$MoH_4(dpe)_2$	Ar	none	8	30
trans-$Mo(N_2)_2(dpe)_2$	Ar	none	1	38
trans-$Mo(N_2)_2(dpe)_2$	H_2	none	20	2
trans-$Mo(N_2)_2(dpe)_2$	H_2	2-propanol	17	2
trans-$Mo(N_2)_2(dpe)_2$	Ar	2-propanol	35	57

[a] Catalyst (0.02 M) and 1-hexene (0.5 M) were heated in toluene (5 ml) at 80 ± 0.1 °C for 1 h. 2-Propanol = 0.75 M, H_2 = 101 kPa. A reactor with a 100 ml interior volume was used.

[b] Based on 1-hexene used.

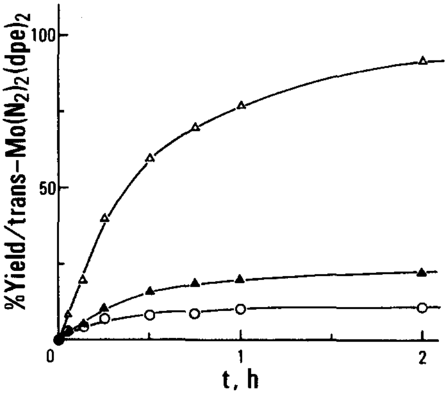
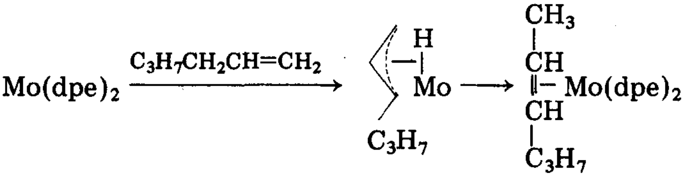


Fig. 2. Time course of the reaction of 1-hexene with *trans*-$Mo(N_2)_2(dpe)_2$ in toluene at 80 ± 0.1 °C. [*trans*-$Mo(N_2)_2(dpe)_2$] = 2.0×10^{-2} M; [1-hexene] = 4.0×10^{-2} M; ○, hexane; △, *trans*-2-hexene; ▲, *cis*-2-hexene.

proposed in the flash photolysis study of *trans*-$W(N_2)_2(dpe)_2$ [18]. Since $Mo(dpe)_2$ has a formerly 14-electron molybdenum atom, the possibility of solvent coordination is present. Furthermore, the $Mo(dpe)_2$ species may contain a Mo—C linkage and be formulated as $MoH(dpe)(C_6H_4PhPCH_2CH_2PPh_2)$. As shown in Table 1, trace amounts of hexane were formed in the reaction of *trans*-$Mo(N_2)_2(dpe)_2$ with 1-hexene, suggesting that the hydrogen may be derived from dpe. Transfer of hydrogen between the organic groups of phosphine ligands and cyclopentene has been reported for a Rh complex [3a]. The reaction of allyl and vinyl carboxylates with *trans*-$Mo(N_2)_2(dpe)_2$ affords propene and ethene, respectively, with *ortho*-metallated complexes [19]. In the presence of 2-propanol, however, the transfer from dpe appears to be incidental to the main reaction.

$$trans\text{-}Mo(N_2)_2(dpe)_2 \underset{N_2}{\overset{-N_2}{\rightleftarrows}} Mo(N_2)(dpe)_2 \underset{N_2}{\overset{-N_2}{\rightleftarrows}} Mo(dpe)_2 \tag{2}$$

Byrne *et al.* have confirmed the formation of Mo(η^3-propenyl)H(dpe)$_2$ by NMR, and have shown that this complex is in dynamic equilibrium with the corresponding zero-valent propene complex [20]. The isomerization of 1-hexene in the absence of 2-propanol is likely to proceed by a similar mechanism involving oxidative addition of an α-CH bond of the olefin to Mo(dpe)$_2$ (eqn. (3)) [21, 22]. However, we could obtain no NMR evidence for the formation of such η^3-allyl hydride-type species. The finding that transfer hydrogenation of 1-hexene was accompanied by double bond migration is noteworthy in this connection. As will be discussed below, it appears that the double bond migration of 1-hexene in the presence of 2-propanol proceeds by a mechanism different from that in the absence of 2-propanol.



(3)

In the reaction of 1-hexene with MoH$_4$(dpe)$_2$, the amount of hydrogen coordinated to molybdenum can be estimated from the hydrogen in the form of hydride ligands, evolved molecular hydrogen, and hydrogen transferred to olefins:

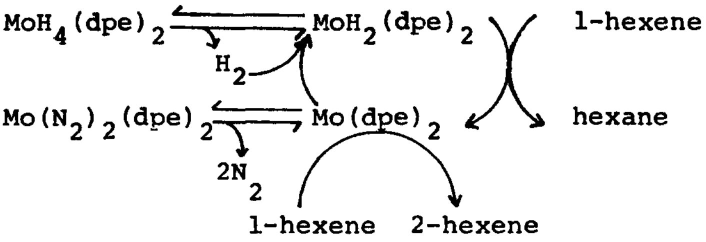
$$[\mathrm{H}\{\mathrm{MoH_2(dpe)_2}\}] = [\mathrm{H}\{\mathrm{MoH_4(dpe)_2}\}]_0 - [\mathrm{H(gas\ phase\ H_2)}] - [\mathrm{H(transferred)}]$$

It was assumed that MoH$_2$(dpe)$_2$ is the only hydrogen-containing species. Thus the amount of Mo(dpe)$_2$ is tentatively evaluated by:

$$[\mathrm{Mo(dpe)_2}] = [\mathrm{MoH_4(dpe)_2}]_0 - [\mathrm{MoH_2(dpe)_2}]$$

The time-course of the double bond migration is consistent with the change in the estimated amount of Mo(dpe)$_2$, as shown in Fig. 1.

The results obtained by the reaction of 1-hexene with MoH$_4$(dpe)$_2$ and *trans*-Mo(N$_2$)$_2$(dpe)$_2$ can be interpreted in terms of the mechanism outlined in Scheme 1. The initial step in the reaction of MoH$_4$(dpe)$_2$ is thought to involve elimination of H$_2$ to form MoH$_2$(dpe)$_2$, followed by coordination of



Scheme 1.

1-hexene and subsequent formation of hexane and $Mo(dpe)_2$.* If H_2 still remains in the atmosphere, it will react preferentially with $Mo(dpe)_2$ to regenerate $MoH_2(dpe)_2$, suppressing the double bond migration caused by $Mo(dpe)_2$. Since *trans*-$Mo(N_2)_2(dpe)_2$ can afford $Mo(dpe)_2$ directly, the double bond migration occurs with no induction period.**

From the mechanism depicted in Scheme 1, one might expect that 1-hexene would be reduced by molecular hydrogen without double bond migration. On using 1 atm of molecular hydrogen instead of 2-propanol, the reduction proceeded moderately without much 2-hexene formation (Table 1). When 2-propanol was added to this 1-hexene–H_2 system, double bond migration still scarcely occurred and no dehydrogenation of 2-propanol was observed. These results indicate no participation of 2-propanol in the reaction in the presence of H_2. It can be seen from Table 1 that molecular hydrogen showed less olefin-reducing ability than 2-propanol, which may be ascribed to the unfavorable shift of the equilibrium in eqn. (1).

Reaction of $Mo(C_2H_4)_2(dpe)_2$ with hydrogen donors

To confirm the possibility of the 'unsaturate' route in the transfer hydrogenation, that is, the mechanism involving the reaction of hydrogen donors with an olefin complex, the reaction of $Mo(C_2H_4)_2(dpe)_2$ with several hydrogen donors was investigated. When dissolved in benzene at 80 °C under Ar prior to addition of donors, $Mo(C_2H_4)_2(dpe)_2$ released 1.0 molar equiv of C_2H_4, suggesting the formation of a five-coordinate complex, $Mo(C_2H_4)(dpe)_2$. Addition of 2-propanol led to the formation of C_2H_6 with a concomitant decrease in vapor-phase C_2H_4 (Fig. 3). After 2 h, 181% of C_2H_6 relative to the initial amount of molybdenum complex was formed. With respect to the reaction path, this finding is consistent with the sequence in eqn. (4).

$$Mo(C_2H_4)_2(dpe)_2 \xrightleftharpoons{-C_2H_4} Mo(C_2H_4)(dpe)_2 \xrightleftharpoons[C_2H_4]{\text{2-propanol}} Mo(dpe)_2 + C_2H_6 \qquad (4)$$

Figure 3 shows that a different behavior occurred when pyrrolidine was used as a hydrogen donor. On addition of pyrrolidine, the amount of gas-phase C_2H_4 instantaneously increased. This is attributed to the preferential coordination of pyrrolidine to molybdenum, displacing the C_2H_4 ligand. Ethane was obtained in only low yield, as was also the case for tetrahydrofuran. Thus pyrrolidine and tetrahydrofuran were unsuitable as the hydrogen donor, although they can donate hydrogen to *trans*-$Mo(N_2)_2(dpe)_2$ to give $MoH_4(dpe)_2$ [13]. Methanol and ethanol had slight hydrogen donating abilities to $Mo(C_2H_4)_2(dpe)_2$. These primary alcohols reacted with the complex to give principally *trans*-$Mo(CO)(N_2)(dpe)_2$ [19] and C_2H_4. The

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*Hydrogenation with molybdenum hydrides has been reported [23].

**Photoassisted hydrogenation systems using $Mo(CO)_6$ and $W(CO)_6$ are accompanied by double bond migration of olefins [24].

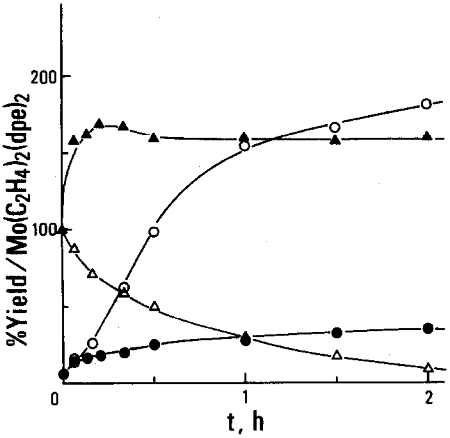


Fig. 3. Time course of the reaction of hydrogen donors with $Mo(C_2H_4)_2(dpe)_2$ in benzene at 80 ± 0.1 °C. $[Mo(C_2H_4)_2(dpe)_2] = 2.0 \times 10^{-2}$ M; [donor] = 6.0×10^{-1} M; donor = 2-propanol: ○, C_2H_6; △, C_2H_4; donor = pyrrolydine: ●, C_2H_6; ▲, C_2H_4.

pertinent data are shown in Table 2. On using 1 atm of molecular hydrogen, 90% C_2H_6 (relative to the initial amount of molybdenum complex) and 102% C_2H_4 remained, and the complex was converted to $MoH_4(dpe)_2$ after 2 h. Thus 2-propanol was superior to H_2 as the reductant of the C_2H_4 ligand.

TABLE 2

The reaction of $Mo(C_2H_4)_2(dpe)_2$ with donors[a]

Donor	Yield (%)[b]	
	C_2H_4	C_2H_6
2-propanol	9	181
methanol	156	34
ethanol	150	33
pyrrolidine	160	35
tetrahydrofuran	149	27
H_2	102	90

[a] A benzene (5 ml) solution of $Mo(C_2H_4)_2(dpe)_2$ (0.02 M) and a donor (0.6 M) was heated at 80 ± 0.1 °C.

[b] Based on the Mo complex.

Comparison of molybdenum and tungsten complexes

As previously described, the reaction of *trans*-$Mo(N_2)_2(dpe)_2$ with 2-propanol afforded $MoH_4(dpe)_2$ and acetone [13]. In the course of the reaction, molecular hydrogen was observed in the atmosphere, consistent with the observation that $MoH_4(dpe)_2$ releases H_2 to give $MoH_2(dpe)_2$. The coordinatively unsaturated species, $MoH_2(dpe)_2$, is predominant above 80 °C and is expected to react with 2-propanol to regenerate $MoH_4(dpe)_2$, thereby establishing a catalytic cycle for the dehydrogenation.

$$\textit{trans}\text{-Mo}(N_2)_2(\text{dpe})_2 + 2\ \text{2-propanol} \longrightarrow \text{MoH}_4(\text{dpe})_2 + 2\ \text{acetone}$$

$$\begin{cases} \text{MoH}_4(\text{dpe})_2 \rightleftharpoons \text{MoH}_2(\text{dpe})_2 + H_2 \\ \text{MoH}_2(\text{dpe})_2 + \text{2-propanol} \rightleftharpoons \text{MoH}_4(\text{dpe})_2 + \text{acetone} \end{cases}$$

As can be seen from Table 3, however, only 2.6 mol 2-propanol per mol equiv molybdenum was dehydrogenated at 80 °C in toluene in 2 h. Evolution of 1.20 mol equiv of H_2 was observed. The addition of 1-hexene enhanced the rate of dehydrogenation of 2-propanol to give a mixture of acetone and hexane, whereas evolution of H_2 was retarded. The effect of cyclohexanone was greater; the rate of dehydrogenation of 2-propanol was enhanced, the evolution of H_2 being negligible. Thus transfer hydrogenation occurred smoothly from alcohols to olefins and ketones by using *trans*-$\text{Mo}(N_2)_2(\text{dpe})_2$.

TABLE 3

Effect of addition of acceptors to Mo and W systems[a]

Catalyst	Acceptor	Yield (mmol)		
		Acceptor hydrogenated	2-Propanol dehydrogenated	H_2 evolved
Mo	none	—	0.26	0.12
Mo	1-hexene	1.03	1.18	0.062
Mo	cyclohexanone[b]	2.17	2.20	0.006
W	none	—	0.20	0.065
W	1-hexene	0.027	0.027	0.0
W	cyclohexanone[b]	0.0	0.0	0.0

[a] Catalyst (0.10 mmol), 2-propanol (3 mmol) and 1-hexene (2 mmol) or cyclohexanone (3 mmol) in toluene (4 ml) were heated at 80 ± 0.1 °C under Ar for 2 h. Catalyst: with Mo, *trans*-$\text{Mo}(N_2)_2(\text{dpe})_2$; with W, *trans*-$\text{W}(N_2)_2(\text{dpe})_2$.

[b] Benzene was used as a solvent.

The tungsten analog, *trans*-$\text{W}(N_2)_2(\text{dpe})_2$ also reacts with 2-propanol to yield $\text{WH}_4(\text{dpe})_2$ [12] and molecular hydrogen; 2.0 mol of 2-propanol per mol tungsten were dehydrogenated in 2 h. On addition of 1-hexene and cyclohexanone, the extent of dehydrogenation decreased to one-eighth of its former value and zero, respectively, and the evolution of H_2 ceased. Thus these acceptors did not at all enhance the dehydrogenation rate of 2-propanol in the tungsten system, as tungsten complex is a poor catalyst for transfer hydrogenation. This result may be explained by the preferential coordination of the acceptors to the tungsten atom.

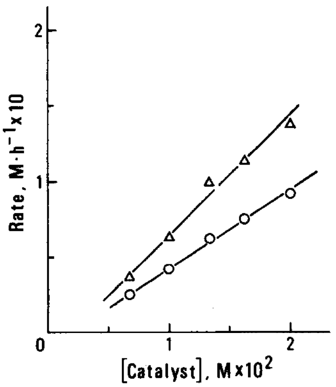
Kinetic results

For kinetic measurements we chose the reduction of 1-hexene with 2-propanol (eqn. (5)) in the presence of *trans*-$\text{Mo}(N_2)_2(\text{dpe})_2$ as catalyst. Unless otherwise noted, the reaction was carried out under standard conditions in

$$\text{1-hexene} + \text{2-propanol} \longrightarrow \text{hexane} + \text{acetone} \ (+ \textit{cis/trans}\text{-2-hexene}) \qquad (5)$$

which *trans*-$Mo(N_2)_2(dpe)_2$ (0.013 M), 1-hexene (0.33 M), and 2-propanol (0.50 M) were heated in toluene under Ar at 80 °C. Double bond migration leading to *trans*- and *cis*-2-hexene was concomitant with the reduction. Subsequent reduction of 2-hexenes was negligible since (i) the reduction of 2-hexene was much slower than that of 1-hexene and (ii) at the initial stage of the reaction the concentration of 2-hexene was small. Treatment of 2-hexene (*trans*/*cis* = 0.23) with *trans*-$Mo(N_2)_2(dpe)_2$ and 2-propanol under our standard conditions revealed that the *cis–trans* geometrical isomerization was very slow in the catalyst system. The concentrations of hexane and *trans*- and *cis*-2-hexene were proportional to reaction time up to 20% conversion. The initial rates were derived from the linear portions of the curves. The dependence of the rates of formation of hexane and *trans*-2-hexene (r_h for hexane and r_t for *trans*-2-hexene) on the concentrations of the catalyst, of 1-hexene, and of 2-propanol, and on temperature was investigated. The dependence of the rate of formation of *cis*-2-hexene was not investigated, since the rate was very small.

Figure 4 shows the dependence of the formation rates on catalyst concentration. Both the dependences were first-order in the region of catalyst concentration above 0.0065 M. As shown in Fig. 5, the initial rate of hexane formation was independent of 1-hexene concentration. The zero-order dependence may be interpreted either by the assumption that the coordination of the olefin to the metal occurs after the rate-determining step or by the assumption that the olefin coordinates so completely as to show a levelling effect, as it does before the rate-determining step. The former assumption seems to be more plausible, because no complex of 1-hexene was



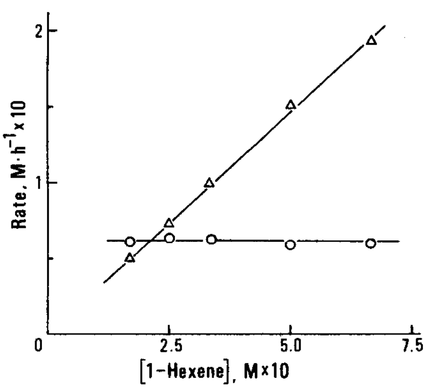


Fig. 4. The dependence of the initial rate on catalyst concentration in toluene at 70 ± 0.1 °C. [1-hexene] = 3.3×10^{-1} M; [2-propanol] = 5.0×10^{-1} M; ○, hexane; △, *trans*-2-hexene.

Fig. 5. The dependence of the initial rate on the concentration of 1-hexene in toluene at 70 ± 0.1 °C. [catalyst] = 1.33×10^{-2} M; [2-propanol] = 5.0×10^{-1} M; ○, hexane; △, *trans*-2-hexene.

obtained either in the presence or in the absence of 2-propanol. On the contrary, the rate of *trans*-2-hexene formation showed a linear dependence on 1-hexene coordination, the rate-determining step occurring after the coordination of 1-hexene. As shown in Fig. 6, the rates of formation of hexane and *trans*-2-hexene were first order in 2-propanol concentration.

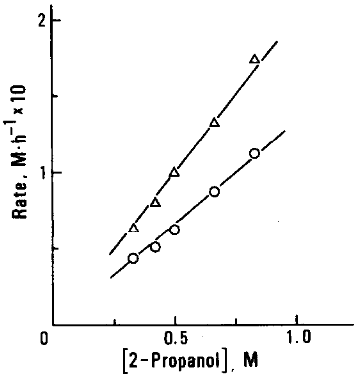
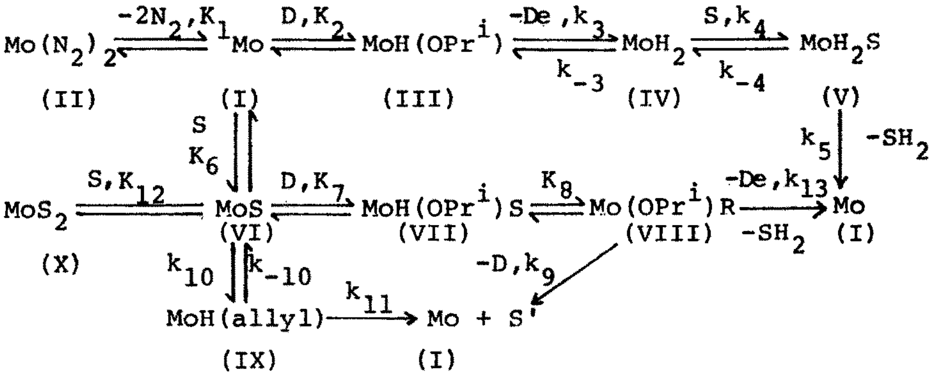


Fig. 6. The dependence of the initial rate on the concentration of 2-propanol in toluene at 70 ± 0.1 °C. [catalyst] = 1.33×10^{-2} M; [1-hexene] = 3.3×10^{-1} M; ○, hexane; △, *trans*-2-hexene.

Initial rates were measured over the range 60 to 95 °C. A good linear plot of $\ln r_h$ versus $1/T$ was obtained, from which a value of the activation energy of hexane, E_{a_h}, of 27 kcal mol^{-1} was calculated. The activation energy of *trans*-2-hexene (E_{a_t}) was 35 kcal mol^{-1}. In order to determine the rate-determining step, an isotopic study was carried out. The k_H/k_D values for the reduction of 1-hexene under our standard conditions, using $(CH_3)_2CHOD$ and $(CD_3)_2CDOD$, were 1.1 and 1.9, respectively. These results suggest that α-hydrogen abstraction may be involved in the rate-determining step. In the double bond migration in the presence of $(CH_3)_2CHOD$ and $(CD_3)_2CDOD$, the isotopic effect was 1.0 and 1.1, respectively. As the rate of double bond migration has a first-order dependence on 2-propanol concentration, the rate-determining step occurs after the transfer of hydrogen(s) from 2-propanol to the metal.

Kinetic discussion

Two pathways are plausible with respect to the transfer hydrogenation: the hydride route (Scheme 1) and the 'unsaturate' route (of the eqn. (4) type). The mechanism of the double bond migration may be either an η^3-allyl hydride mechanism (eqn. (3)) or a σ-alkyl mechanism via the intermediate common with the transfer hydrogenation. Taking into account these mechanisms, we should like to propose Scheme 2 for the catalytic cycle of transfer hydrogenation and double bond migration. The behavior of 1-hexene toward $MoH_4(dpe)_2$ described above shows that double bond



dpe ligands are omitted for clarity; D = 2-propanol, S = 1-hexene, S′ = 2-hexene, De = acetone, R = alkyl.

Scheme 2.

migration via the dihydrido–olefin complex V can be neglected. Based on the proposed Scheme and the assumption described later, r_t and r_h are expressed as follows, respectively:

$$r_t = \frac{K_1K_6[S][C]_0\{K_7K_8k_9[D] + k_{10}k_{11}/(k_{-10} + k_{11})\}}{[N_2]^2 + K_1 + K_1K_2[D] + K_1K_6[S] + K_1K_6K_7(1 + K_8)[S][D] + K_1K_6K_{12}[S]^2} \tag{6}$$

$$r_h = \frac{K_1[S][D][C]_0[K_2k_3k_4k_5/\{k_4k_5[S] + k_{-3}[De](k_{-4} + k_5)\} + K_6K_7K_8k_{13}]}{[N_2]^2 + K_1 + K_1K_2[D] + K_1K_6[S] + K_1K_6K_7(1 + K_8)[S][D] + K_1K_6K_{12}[S]^2} \tag{7}$$

where K_1, K_2, K_6, K_7, K_8 and K_{12} are equilibrium constants and k_3, k_{-3}, k_4, k_{-4}, k_5, k_9, k_{10}, k_{-10}, k_{11} and k_{13} are rate constants and [D], [S], $[C]_0$, [De] and $[N_2]$ are the concentrations of 2-propanol, 1-hexene, the added catalyst, acetone, and dinitrogen, respectively. The assumption is that the hydride species IV and V, and the allyl hydride species IX are so active that steady-state treatment can be applied. This assumption seems conceivable, because the spectrometric study of this reaction system showed no sign of the existence of such hydride species.

As r_t has a first-order dependence on 2-propanol concentration, the following relations should be satisfied by eqn. (6):

$$K_7K_8k_9[D] \gg k_{10}k_{11}/(k_{-10} + k_{11});$$

$$[N_2]^2 + K_1 + K_1K_6[S] + K_1K_6K_{12}[S]^2 \gg K_1K_2[D] + K_1K_6K_7(1 + K_8)[S][D]$$

The former relation requires that in the presence of 2-propanol the σ-alkyl mechanism via compound VIII is preferred in the double bond migration; this is consistent with the observation that the rate of the double bond migration in the absence of 2-propanol is much slower than in the presence of 2-propanol [25]. The rate expression becomes as follows (eqn. (8)).

$$r_t = \frac{K_1K_6K_7K_8k_9[S][D][C]_0}{[N_2]^2 + K_1 + K_1K_6[S] + K_1K_6K_{12}[S]^2} \tag{8}$$

Then, as the rate has a first-order dependence on 1-hexene concentration, the following relation should be satisfied by eqn. (8):

$[N_2]^2 + K_1 \gg K_1K_6[S] + K_1K_6K_{12}[S]^2$

These relations are rewritten as follows:

$[N_2]^2 + K_1 \gg K_1K_2[D] + K_1K_6[S] + K_1K_6K_7(1 + K_8)[S][D] + K_1K_6K_{12}[S]^2$

i.e.,

$[I] + [II] \gg [III] + [VI] + [VII] + [VIII] + [X]$.

Then the rate expression becomes:

$$r_t = \frac{K_1K_6K_7K_8k_9[S][D][C]_0}{[N_2]^2 + K_1} \tag{9}$$

By introducing the assumption above, the rate expression for r_h becomes as follows:

$$r_h = \frac{K_1[D][C]_0(K_2k_3 + K_6K_7K_8k_{13}[S])}{[N_2]^2 + K_1} \tag{10}$$

As the rate r_h has a zero-order dependence on 1-hexene concentration, $K_6K_7K_8k_{13}[S]$ must be so small as to be negligible compared to K_2k_3. This means that the 'hydride' route prevails in the transfer hydrogenation of 1-hexene. As described earlier, the reaction of $Mo(C_2H_4)_2(dpe)_2$ with 2-propanol suggests that the 'unsaturate' mechanism may be operative in the case of ethylene. However, the tendency of 1-hexene to coordinate to the molybdenum atom is lower than that of ethylene. While *trans*-$Mo(N_2)_2(dpe)_2$ is readily converted into $Mo(C_2H_4)_2(dpe)_2$ on exposure to ethylene, it is recovered unchanged from the reaction with 1-hexene. These results are compatible with the 'hydride' route, in which reaction with 2-propanol giving the hydride IV precedes 1-hexene coordination. And hexane would be produced by way of a hydridoalkyl intermediate, as postulated in homogeneous catalytic hydrogenations [26]. Equation (10) is reduced to:

$$r_h = \frac{K_1K_2k_3[D][C]_0}{[N_2]^2 + K_1} \tag{11}$$

Comparison of eqns. (9) - (11) shows that the relation $k_9 \gg k_{13}$ should be held. Thus although there should be competition by 1-hexene for the active species I, it is believed to be external to the catalytic cycle of transfer hydrogenation, leading to the double bond migration. In eqn. (11), k_3 is the only rate constant and the most important step, and therefore the dehydrogenation step III → IV should be rate-limiting in the transfer hydrogenation. This supposition is supported by the results of studies of the kinetic isotope effects, which indicate that α-hydrogen abstraction may be involved in the rate-limiting step. Equations (9) and (11) are found to accommodate the fact that the presence of dinitrogen greatly retarded both the transfer hydrogenation and double bond migration [7]. However, we could not investigate in detail the dependence of the rates on the dinitrogen concentration, due to experimental difficulties.

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