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The Kinetics and Mechanism of the Homogeneous Hydrogenation of 1-Hexene Catalyzed by Hydridotetrahydroboratotris-(triphenylphosphine)ruthenium(II)

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The first detailed kinetic study of a hydrogenation catalyzed by a metal-coordinated BH_4–phosphine complex is reported. The kinetics of the hydrogenation of 1-hexene in benzene at 20°C, at atmospheric pressure and catalyzed by $RuH(BH_4)(PPh_3)_3$, has been studied, and the reaction proceeds by the unsaturate route, i.e., dissociation of the catalyst, formation of an alkyl complex, and then oxidative addition of hydrogen in a rate-determining step. The activity of this complex is compared with that of other related ruthenium catalysts.

INTRODUCTION

Very little is known about the catalytic properties of tetrahydroborate complexes, compared with the vast amount of information now available on homogeneous hydrogenations catalyzed by, for example, hydrides, carbonyls, halides, and various mixed-ligand complexes of transition metals.

Mixtures of Ni(II) halides or complexes and $NaBH_4$ in solvents such as dimethylformamide (dmf) (*1–3*), ethanol/tetrahydrofuran (*4*), ethanol/benzene (*4*), diglyme (*5*), or ethanol (*6*) are effective catalysts in a variety of hydrogenations and, while the active species have not been identified, it has been suggested (*2*) that coordinated BH_4^- complexes, e.g., $NiCl(BH_4)(dmf)_3$ (*3*), may be involved. The related complex, $RhCl_2(BH_4)py_2(dmf)$ (py = pyridine), obtained from $RhCl_3py_3$ and $NaBH_4$ in dmf (*7*), is also an efficient catalyst in a variety of reactions (*1, 7*). Furthermore, the BH_4^- complex of Co(II), $CoH(BH_4)(PCy_3)_3$ (PCy_3 = tricyclohexylphosphine) (*8*), is an active and selective catalyst for hydrogenation and isomerization reactions.

The only kinetic data available on homogeneous hydrogenations catalyzed by BH_4^- complexes appear to be restricted to the $RhCl_2(BH_4)py_2(dmf)$ system (*7*), in which evidence suggests that the hydrogen and *not* the BH_4^- is involved in the reduction process. That is to say, both the dmf and BH_4^- remain coordinated to the metal throughout the catalytic hydrogenation. Furthermore, added py retards the rate.

As part of our studies of the conditions under which metal–BH_4 complexes can be isolated (9), we have prepared $RuH(BH_4)P_3$ (P = triphenylphosphine) (*10*), which is closely related to the known catalysts $RuCl_2P_3$ (*11*) and $RuHClP_3$ (*12*). As an extension of this work, this paper presents a study of the homogeneous hydrogenation of 1-hexene in benzene at 20°C, catalyzed by $RuH(BH_4)P_3$. The available physical evidence suggests (*10*) that the BH_4^- is present as a monodentate ligand, at least in the solid state, and that the arrangement

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TABLE 1

Summary of Kinetic Data for Hydrogenation of 1-Hexene in Benzene at 20°C

$[RuH(BH_4)P_3]$ ($\times 10^3$ *M*)	$[PPh_3]$ added ($\times 10^3$ *M*)	[1-Hexene] (*M*)	$[H_2]$ ($\times 10^3$ *M*)	Initial rate ($\times 10^5$ *M* s^{-1})
1.00		0.32	4.48	3.61
1.00		0.50	4.48	4.59
1.00		0.85	4.48	8.99
1.00		0.94	4.48	10.25
1.00		1.25	4.48	12.28
1.00		1.57	4.48	14.81
1.00		0.50	1.925	2.28
1.00		0.50	2.25	2.86
1.00		0.50	2.68	3.45
1.00		0.50	3.93	4.78
1.00		0.50	4.68	5.49
1.00		0.50	4.95	5.95
0.15		0.50	4.48	2.77
0.52		0.50	4.48	3.42
1.00		0.50	4.48	4.59
1.67		0.50	4.48	5.02
2.81		0.50	4.48	5.49
3.34		0.50	4.48	5.74
3.80		0.50	4.48	5.82
1.00		0.50	4.48	4.59
1.00	0.54	0.50	4.48	4.08
1.00	1.10	0.50	4.48	3.62
1.00	1.48	0.50	4.48	3.31
1.00	1.95	0.50	4.48	3.18

about the Ru atom is trigonal bipyramidal with three equatorial phosphine ligands. Related work to be reported in a separate publication will concern catalysis by much less stable Ni(I)- and Co(I)-BH_4 complexes.

EXPERIMENTAL METHODS

The air-sensitive complex $RuH(BH_4)P_3$ was prepared in a manner similar to that previously described (*10*) by continuous stirring of a mixture of $RuCl_2P_2$, P, and $NaBH_4$ (in the ratio 1:3:10) in ethanol at room temperature under nitrogen for about 3 hr. The yellow product was collected by filtration, washed in sequence with ethanol, water, ethanol, and ether, and finally recrystallized from benzene and dried under reduced pressure for 3 hr.

Solvents were dried by standard methods described previously (*13*). The apparatus used for the catalytic studies and the detailed method employed for rate measurements have also been described previously for similar experiments concerning Rh(I) complexes (*13*).

RESULTS AND DISCUSSION

Benzene solutions of $RuH(BH_4)P_3$ catalyze the homogeneous hydrogenation of 1-hexene under ambient conditions at approximately one-fourth the rate observed using Wilkinson's catalyst, $RhClP_3$, under similar conditions. Solutions of the catalyst in benzene are reddish brown, but change to yellow brown upon addition of 1-hexene when the catalyst concentration is low (less than $\sim 0.5.10^{-3}$ *M*). At higher concentrations of catalyst, the color change is less apparent. Also, the color of the $RuH(BH_4)P_3$ solution remains unchanged when it is stirred under hydrogen in the absence of

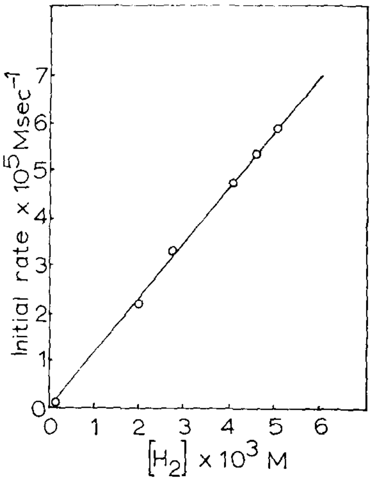


FIG. 1. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on $[H_2]$ (0.5 *M* 1-hexene, 1 m*M* Ru^{II}).

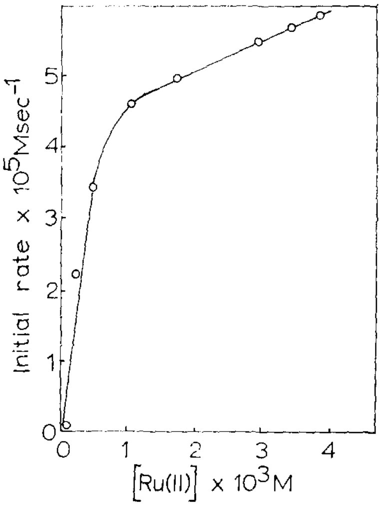


FIG. 3. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on $[Ru^{II}]$ (4.48 m*M* H_2, 0.5 *M* 1-hexene).

added olefin. No uptake of hydrogen is observed in the absence of the catalyst, and no metal was visible in the reaction flask at the end of each experiment.

The reaction was followed by measuring the drop in H_2 pressure, and the initial rate of hydrogenation of 1-hexene was obtained from the tangent to the plot of H_2 uptake against time. Table 1 shows the initial rates of hydrogenation of 1-hexene for a variety of catalyst, 1-hexene, H_2, and phosphine concentrations at 20°C. The reaction is first order in H_2 (Fig. 1) and first order in olefin at low concentrations (<1.0 m*M*); at higher concentrations, a zero-order dependence is observed (Fig. 2). The dependence of the initial rate on catalyst concentration (Fig. 3) is much more complicated. Thus, at concentrations of

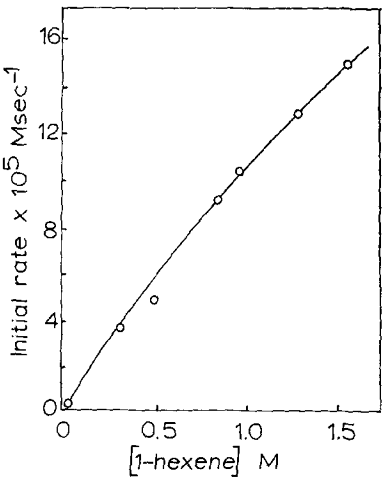


FIG. 2. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on [1-hexene] (4.48 m*M* H_2, 1 m*M* Ru^{II}).

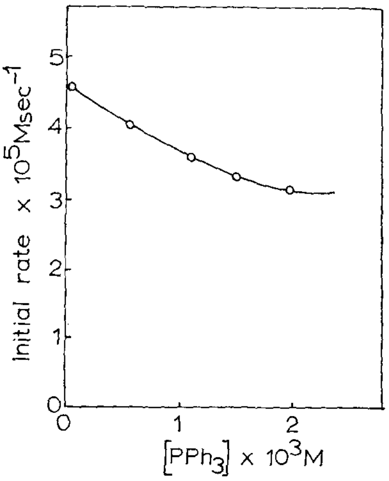


FIG. 4. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on $[PPh_3]$ (4.48 m*M* H_2, 0.5 *M* 1-hexene, 1 m*M* Ru^{II}).

catalyst higher than ~1 m*M*, the dependence is first order, while the apparent higher rate at low concentrations suggests a concentration-dependent change from one active species to another, rather than the lack of solubility of the catalyst. Addition of phosphine retards the reaction (Fig. 4), and a plot of the reciprocal of the rate against triphenylphosphine concentration is linear (Fig. 5). The following hydrogenation mechanism is consistent with these data:

$$RuH(BH_4)P_3 \overset{K_1}{\rightleftharpoons} RuH(BH_4)P_2 + P; \quad (1)$$

$$RuH(BH_4)P_2 + \text{alkene} \overset{K_2}{\rightleftharpoons} Ru(BH_4)(P_2)(\text{alkyl}); \quad (2)$$

$$Ru(BH_4)P_2(\text{alkyl}) + H_2 \xrightarrow{k} RuH(BH_4)P_2 + \text{alkane}. \quad (3)$$

The rate law for this mechanism would be of the form:

$$\text{rate } (R) = \frac{kK_2[\text{alkene}][H_2][RuH(BH_4)P_3]}{1 + K_2[\text{alkene}] + ([P]/K_1)}, \quad (4)$$

and the observed results can be satisfactorily explained with this rate law. At low concentrations of catalyst, further dissociation to give the more active species $RuH(BH_4)P$ apparently takes place.

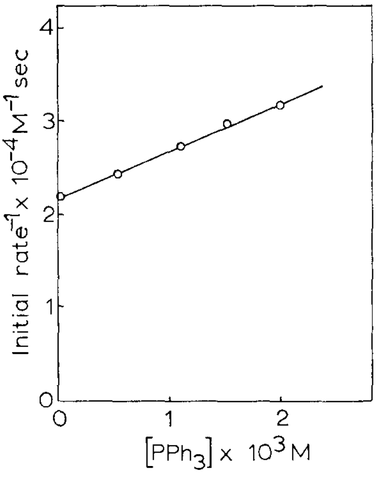


FIG. 5. Inverse dependence of the initial rate of hydrogenation of 1-hexene in benzene at 20°C on $[PPh_3]$ (4.48 m*M* H_2, 0.5 *M* 1-hexene, 1 m*M* Ru^{II}).

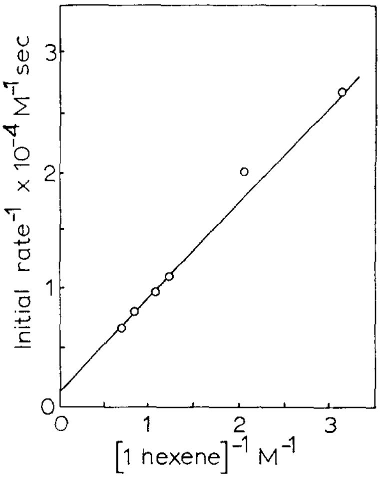


FIG. 6. Plot of 1/rate versus 1/[hexene] according to Eq. (5).

Equation (4) can be rearranged in the form:

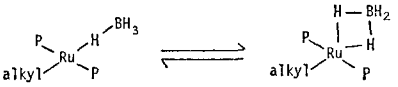
$$\frac{1}{R} = \frac{1 + [P]/K_1}{kK_2[RuH(BH_4)P_3][H_2]}\left(\frac{1}{[\text{alkene}]}\right) + \frac{1}{k[RuH(BH_4)P_3][H_2]}. \quad (5)$$

A plot of $1/R$ versus 1/[alkene] yields a reasonably good straight line (Fig. 6), from the intercept of which k is estimated to be approximately 139 $M^{-1}s^{-1}$. Extensive dissociation of $RuH(BH_4)P_3$ is evident from the dependence of the rate on added triphenylphosphine, and the plot of $1/R$ versus [P] is linear as required by the following equation derived from Eq. (4):

$$\frac{1}{R} = \frac{[P]}{kK_1K_2[H_2][\text{alkene}][RuH(BH_4)P_3]} + \frac{1 + K_2[\text{alkene}]}{kK_2[H_2][\text{alkene}][RuH(BH_4)P_3]}. \quad (6)$$

Due to the limited data available, it is not possible to estimate the exact values of K_1 and K_2. However, from Eqs. (5) and (6), the limiting values can be calculated as $K_1 < 10.4\ M$ and $K_2 > 0.07\ M^{-1}$. From the ratio of intercept to gradient of the plot of $1/R$ against $1/[\text{alkene}]$ (Fig. 6), K_2 is approximately $0.17\ M^{-1}$, which would give a value of $0.12\ M$ for K_1. The catalyst is over 95% dissociated in solution at a $10^{-3}\ M$ concentration, and there is an appreciable amount of alkyl complex formed in solution.

Thus, the behavior of $RuH(BH_4)P_3$ in catalyzing the homogeneous hydrogenation of terminal olefins is closely related to that of the known catalysts $RuHClP_3$ (*12*) and $RuH(CF_3COO)P_3$ (*14*) and involves the mechanism outlined in Eqs. (1)–(3). A detailed discussion of this type of mechanism can be found elsewhere (*15*). The activities of these catalysts decrease in the order: $RuHClP_3 > RuH(CF_3COO)P_3 > RuH(BH_4)P_3$ in the approximate ratio of 100:10:2. The radically different electronic properties of Cl^- and BH_4^- probably comprise the most important factor responsible for this large decrease. The deficiency in electron density in the Ru–H bond of the monodentate Ru–H–BH_3 unit (*10*) will cause *d* electrons to flow from the metal ion, thereby decreasing its electron density and rendering the catalyst much less active toward-hydrogen activation [step (3)]. Moreover, in the dilute ($10^{-3}\ M$) solutions of the catalyst, equilibria such as are



possible, and the resulting 5-coordinated species would then be unable to undergo oxidative addition with H_2 to form the octahedral $RuH_2(\text{alkyl})(BH_4)P_2$. Although the BH_4^- group is believed not to be the hydride source in other reactions (*7*), there is no evidence here that all the hydrogen used in the reduction process actually comes from molecular hydrogen. Reactions with added $NaBH_4$ would be very informative, but, unfortunately, these cannot be carried out due to the insolubility of $NaBH_4$ in benzene.

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