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Addition of H_2–D_2 Mixtures to 2-Butyne and Norbornene Catalyzed by Solutions of Chlorotris(triphenylphosphine)rhodium(I), Hydridocarbonyltris(triphenylphosphine)rhodium(I), and Hydridotetrakis(5-phenyl-5-*H*-dibenzophosphole)rhodium(I)[1,2]

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Abstract—The use of H_2/D_2 mixtures in place of H_2 as a probe of the mechanisms of hydrogenation is explored using the catalyst precursors chlorotris(triphenylphosphine)rhodium(I) (**I**), hydridocarbonyltris(triphenylphosphine)rhodium(I) (**II**), and hydridotetrakis(5-phenyl-5-*H*-dibenzophosphole)rhodium (I) (**III**). Benzene solutions of these complexes catalyze the H_2–D_2 equilibration, the relative rates decreasing in the order **III** > **II** > **I**. The accepted mechanism of hydrogenation catalyzed by **I** does not accommodate the observed isotopic exchange, which is inhibited by added acids (trifluoroethanol, 1,3,4-trichlorophenol) and accelerated by small amounts of triethylamine; the formation of hydridotris(triphenylphosphine)rhodium(I) is implicated. The H_2 and D_2 added to an unsaturated hydrocarbon is randomized with complexes **II** and **III** as the catalyst, whereas the molecular identity of H_2 and D_2 is retained if the dihydrido is the catalyst.

In the case that **I** is used as a catalyst, the products of the addition of H_2/D_2 mixtures to either 2-butyne or norbornene when catalyzed by **II** or **III** contain the expected random distributions of the added H/D; however, the proportion of randomized addition relative to the addition in which the molecular identity of the addendum (H_2, D_2, HD) is retained depends upon the conditions and the particular unsaturated substrate. Consideration of the kinetic isotope effects for addition indicates that, in forming the randomized product, the H_2–D_2 equilibration proceeds via the dihydride catalytic cycle.

The use of H_2–D_2 mixtures in place of dihydrogen can furnish important clues as to the mechanism of hydrogenation, indicating whether catalysis is heterogeneous or homogeneous [1–6]. The infrequent use of this technique in homogeneous catalysis reflects the greater ease of observing intermediates and interpreting reaction kinetics in homogeneous as opposed to heterogeneous systems. We believe, however, that systematic studies of this kind with representative soluble complexes, whose mechanisms of catalysis are well established, will make it possible to better apply to heterogeneous systems mechanistic insights that have been gained from homogeneous systems. To this end, for our initial studies, we selected chlorotris(triphenylphosphine)rhodium(I) (**I**), hydridocarbonyltris(triphenylphosphine)rhodium(I) (**II**), and hydridotetrakistri(5-phenyldibenzophosphole)rhodium(I) (**III**), which are precursors, respectively, of dihydride (**I**) [7, 8] and monohydride (**II** and **III**) hydrogenation catalysts [9].

In their first comprehensive report on the catalytic properties of complex **I**, Osborn, Jardin, Young, and Wilkinson showed that the reaction of H_2–D_2 mixtures with 1-hexene gave mainly C_6H_{14} and $C_6H_{12}D_2$ accompanied by small amounts of $C_6H_{13}D$, which increased with increasing total pressure [3]. The retention of the molecular identity of H_2 (D_2) in the products supported their proposed mechanism; however, the appearance of HD and monodeuterohexane was not well explained. Schrock and Osborn employed H_2–D_2 mixtures as well as D_2 in studies of the cationic complex $[Rh(NBD)(P(OPh)_3)_2]^+ PF_6^-$ as a catalyst precursor for the hydrogenation of 1-hexene and concluded that both dihydride and monohydride species were present in the solution (Eq. (I)) [4]:

$$[RhH_2L_nS_x]^+ \longrightarrow RhHL_nS_y + H^+. \qquad (I)$$

We will show that a similar situation arises in solutions of $ClRh(PPh_3)_3$ and that the contribution of each type of catalytic species to the products of the reaction can be estimated by the use of H_2–D_2 mixtures. To accomplish this, we employ methods that have been exploited in studies of heterogeneous catalysis [10].

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[1] This article was submitted by the authors in English.
[2] The experiments were conducted at the University of Arkansas.
† Deceased.

The unsaturated hydrocarbons 2-butyne and norbornene were chosen for convenience in performing the planned experiments and to simplify the analysis of the results. Other alkynes and alkenes were used to facilitate comparisons with the reports of other investigators [5].

EXPERIMENTAL

Materials. Hydrogen and deuterium were diffused through palladium alloy cells into storage bulbs. Benzene was distilled from sodium diphenyl–ketyl and transferred to its storage vessel via syringe. The benzene was subjected to a series of freeze–pump–thaw cycles before it was transferred to the reactor. 2-Butyne and norbornene were first purified by preparative chromatography and then distilled from metallic potassium into sampling bulbs, which were attached to an appropriate inlet to the reactor manifold. These too were degassed via freeze–pump–thaw cycles before use.

Hydridotetrakis(5-phenyl-5-*H*-dibenzophosphole)rhodium(I), $[HRh(DBP)_4]$ [11], hydridocarbonyltris(triphenylphosphine)rhodium(I), $[HRhCO(PPh_3)_3]$ [12], tris(triphenylphosphine)chlororhodium(I), $PhCl(PPh_3)_3$ [3], and cyclooctadiene–rhodium(I) chlorine, $[Rh(COD)Cl]_2$ [13] were prepared according to the literature.

Apparatus and procedures. Experiments were performed in a gas recirculating batch reactor similar in principle to the one described by Yasumori and Hirabayashi [14]. The apparatus incorporates a metal bellows pump (Metal Bellows Corp., model MB-21) in the recycle loop that can either include or bypass the detachable reaction vessel, which is fitted with a septum closed inlet. A gas expansion chamber follows the reaction vessel in the recycle loop, having connections to gas and solvent storage vessels; a gas sampling manifold; a flowmeter, which can be included in the loop as desired; a manometer; and vacuum pumps (mechanical and diffusion). The reaction vessel contains a magnetic stirring bar and is immersed in a temperature-controlled water bath (15 ± 0.1°C). Vacuum-line techniques are used to transfer 2-butyne, norbornene, and benzene from their reservoirs to the reaction vessel. Less volatile solvents or unsaturated hydrocarbons are introduced through the septum using a gas tight syringe. A weighed portion of the catalyst precursor is placed in the reaction vessel before it is attached to the recycle loop. The system is evacuated for 1 h to remove free and adsorbed air from the reactor and the catalyst precursor before transferring solvent or reactant to the reaction vessel.

Analytical methods. To determine the ratio $H_2 : HD : D_2$, samples of the vapor are drawn into an evacuated elbow of the gas sampling manifold, where the condensable vapors are trapped (cooled by liquid nitrogen). A portion of the gas sample is expanded into the sampling loop, from which it is carried in a stream of helium through a column (1/8 in. × 10 ft) of manganous chloride (10%) treated alumina; cooled by liquid nitrogen to separate the mixture into its components; and then through a tube containing cupric oxide (400°C to form H_2O, HOD, and D_2O, respectively); and, finally, through the thermal conductivity detector of a gas chromatograph (Varian A-90-P3) [15]. To analyze the liquid phase, a sample of the solution is withdrawn through the septum by syringe and injected into a gas chromatograph (Hewlett-Packard Model 5720A) equipped with a flame ionization detector. The following columns were used: (a) 1/8" × 10' 20% bis(methoxyethyl)adipate on Chromosorb P 80/100 at 50°C (products of 2-butyne and hexynes); (b) 1/8" × 10' 15% SE-30 (methyl) on Chromosorb PAW 80/100 at 80°C (products of norbornene). To provide a sample for mass spectral analysis, the products in a larger sample were separated using a Varian Aerograph (model A-90-P) with a thermal conductivity detector with column (c) 1/4" × 10' 20% bis(methoxyethyl)adipate on Chromosorb P 60/80 at 50°C (products of 2-butyne and hexynes); or (d) 3/8" × 20' 20% Carbowax 750 on Chromosorb PAW at 50°C (products of norbornene). The low boiling hydrocarbons (products of 2-butyne) are collected in a receiver, which can be attached by means of a simple adapter to the gas sampling inlet of the mass spectrometer. The higher boiling point hydrocarbons are collected in small tubes, which can be connected to the mass spectrometer via a modified sampling system. The isolated hydrocarbons are analyzed with the Hitachi–Perkin Elmer RMU-6 E mass spectrometer at a low ionization voltage (8 eV) to minimize fragmentation. The isotopic distribution of the various deuteromolecules is determined from the parent ion (P^+) peaks after corrections for the naturally occurring ^{13}C and ^2H.

Treatment of data. (a) The rates of the H_2/D_2 equilibration were obtained graphically from plots of Eq. (1), where N is the total number of molecules (H_2, HD, D_2)

$$-N\ln(F_e^{HD}-F_t^{HD})/(F_e^{HD}-F_0^{HD}) = Rt \qquad (1)$$

in the system and F_e^{HD}, F_t^{HD}, and F_0^{HD} are the mole fractions of HD at equilibrium, time t, and, initially, R is expressed as moles formed per minute for the amount of catalyst recorded [2].

The rate of formation of HD is related to R through Eq. (2), where P_{HD}, P_{H_2}, and P_{D_2}

$$\frac{N\,\mathrm{d}P_{HD}}{\mathrm{d}t} = \frac{R2P_{H_2}P_{D_2}}{P}, \qquad (2)$$

P_{D_2} represent the partial pressures of HD, H_2, and D_2, and P the total pressure; consequently, at equal pressures of H_2 and D_2, the initial rate of forming HD is $R/2$. For easy comparison with the rate of addition of hydrogen, the entries in Tables 1, 2, and 4 are given as $R/2$, which represents the initial rate of forming HD in the system.

Table 1. The effect of various additives on the initial H_2–D_2 equilibration rate catalyzed by $ClRh(PPh_3)_3$ in benzene at 15°C*

Additive	$R/2 \times 10^6$, mol/s
–	0.40
Triethylamine	0.53
Perchloric acid	0.11
Hydroquinone	0.12
2,4,5-Trichlorophenol	0.04
Trifluoroethanol**	0.69
Trifluoroethanol** and perchloric acid	0.13

* $[ClRh(PPh_3)_3] = (2.3 \pm 0.1) \times 10^{-3}$ M in 50 mL benzene; [Additive] = 20 mol % of [Rh], $D_2 : H_2 = 1 : 1$, $D_2 + H_2 =$ 0.040 mol.

** Benzene : trifluoroethanol = 4 : 1.

The rates of hydrogen addition were obtained graphically from the slopes of first-order plots of the conversion of 2-butyne or norbornene, respectively. Because the reaction system has a fixed volume, both hydrogen addition and sampling of the gas phase reduce the pressure, but these effects upon the apparent first-order rate constants were minimized through an extrapolation of the plots to initial conditions. The initial rate of forming the addition product is obtained by multiplying the first-order rate constant by the moles of the unsaturated hydrocarbons initially present in the system and is so recorded in the tables.

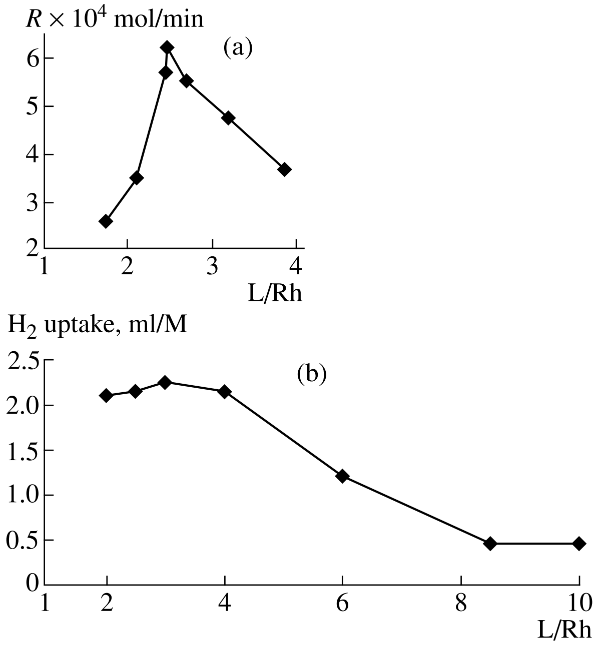


Fig. 1. (a) Rate of H_2–D_2 equilibrium in benzene at 15°C and 1.0 atm. Various amounts of P(*p*-tolyl)$_3$ in a solution of $[Rh(COD)Cl]_2$. (b) Rate of hydrogenation uptake by 10 ml of 1.0 M cyclohexene in toluene at ambient temperature and 1.0 atm. Various amounts of P(*p*-tolyl)$_3$ in a solution of {RhCl[P(*p*-tolyl)$_3$]$_2$}$_2$.

To abstract a measure of the kinetic isotope effect from the mass spectrometric analysis, the random distributions were calculated using the binomial formula assuming that each of the two positions gained D or H in proportion to the probability of transferring D or H (a/b) to each position. The fraction of molecules with m deuterium atoms and s hydrogen atoms ($m + s = 2$) is given by $d_m(2)$ (Eq. (3)). The observed average deuterium content of the product provides a check on the correct value of a/b [10]:

$$d_m = \frac{(a/b)^m 2!}{(1 + a/b)^2 m! s!}. \tag{3}$$

For results in which the distributions were partly random (with $ClRh(PPh_3)_3$ as the catalyst), the nonrandom distribution was assumed to result from the addition of H_2 and D_2 in proportion to the directly observed kinetic isotope effect. The mole fraction of each mode of addition is designated as N_2 and N_A, respectively ($N_2 + N_A = 1$).

RESULTS

H_2/D_2 equilibration. In accordance with previous reports, benzene solutions of the monohydride complexes catalyze the H_2/D_2 equilibration, the complex $HRh(DBP)_4$ being somewhat more effective than $HRh(CO)(PPh_3)_3$ at the concentrations employed [16]. Benzene solutions of $ClRh(PPh_3)_3$ are less active, the relative reactivity for $HRh(DBP)_4$, $HRh(CO)(PPh_3)_3$, $ClRh(PPh_3)_3$ being approximately 5 : 3 : 1. The presence of norbornene and 2-butyne does not significantly effect the H_2–D_2 equilibrium.

Experiments were conducted in an attempt to identify the cause of the H_2/D_2 equilibration by solutions of $ClRh(PPh_3)_3$ benzene, because the exchange is not explained by the currently accepted mechanisms of the reaction of dihydrogen with this complex. The observations of Osborn, Jardin, Young, and Wilkinson that D_2 does not exchange with any component of the solution and that the rate increases with the concentration of the complex were confirmed [3]. They also noted that this exchange reaction increased with an increase in the total pressure of H_2 plus D_2.

The rate of the H_2/D_2 equilibration is a function of the ratio of phosphine to rhodium, as shown in Fig. 1, in which the catalyst used was prepared *in situ* from the dimer $[Rh(COD)Cl]_2$ and various amounts of tri(3-tolyl)phosphine. The maximum rate occurs at a ratio (L/Rh) of three. The addition of small amounts of acids depresses the rate of equilibration, whereas triethylamine enhances it (Table 1). Of the phenolic inhibitors, 2,4,5-trichlorophenol and *p*-hydroquinone, the stronger acid is the more effective. The acidic alcohol, trifluoroethanol, when used in large amounts (one part by volume to four parts of benzene) gives an increase in rate, but the addition of perchloric acid to the mixed solvent lowers the rate below that in benzene.

The possibility of an exchange reaction between deuterium and the Wilkinson complex or with trifluoroethanol was tested, although no exchange between D_2 and the catalyst in benzene had been found by Wilkinson and coworkers [3, 18] or Biellman and Liesenfelt [19]. Accordingly, the Wilkinson complex was stirred in an atmosphere of D_2 with a mixture of benzene and trifluoroethanol for 24 h; no HD was formed. The effect of acids on the H_2–D_2 equilibration is analogous to the observations of Schrock and Osborn on cationic rhodium complexes, and, in confirmation of the relationship, the addition of triphenylphosphine, dihydrogen, and triethylamine to a benzene solution of $ClRh(PPh_3)_3$ leads to the isolation of $HRh(PPh_3)_4$ [4].

The competitive rates of the H_2–D_2 equilibration and the addition of H_2, D_2, or the HD mixtures to 2-butyne and norbornene are shown in Table 2. Under the conditions examined, the rate of forming HD is greater than the rate of adding H_2 (HD, D_2) except for the reactions involving norbornene and either $HRh(CO)(PPh_3)_3$ (**II**) or $ClRh(PPh_3)_3$ (**I**). The presence of norbornene and 2-butyne does not have a significant effect on the H_2–D_2 equilibrium. At the same time, norbornene hydrogenates more rapidly than 2-butyne, particularly when catalyzed by the monohydride catalyst **II**.

The quantitative significance of the above intercomparisons is limited because the activities for hydrogenation and exchange are neither directly proportional to the formal concentration of the complex nor is the variation with concentration the same function for each complex, the latter being due to the differing number and activity of the catalytic species that are formed upon the dissociation of one or more ligands [11, 20, 21]. The distinction between the catalytic properties of the monohydride and the dihydride catalysts is blurred, because solutions containing the latter (complex **I**) also appear to contain a catalyst of the monohydride type. Nevertheless, the results aid in understanding the variation in the distribution of deuterium in the addition products when H_2–D_2 mixtures are used as a probe of the mechanism of addition.

For comparison with the rate of adding H_2–D_2 mixtures, the rates of adding either D_2 or H_2 are given for the monohydride complexes (Table 3). As expected, both $HRh(DBP)_4$ and $HRh(CO)(PPh_3)_3$ exhibit positive isotope effects for the hydrogenation of 2-butyne or norbornene ranging from 1.5 to 1.8, with an uncertainty of less than 10% as estimated from the reproducibility of repeated rate measurements.

The addition products. (a) 2-Butyne/($HRhL_4$). In the reported experiments, the main product of the hydrogenation of 2-butyne is *cis*-2-butene; at 60% conversion, the geometrical selectivity is greater than 98% *cis*. With $HRh(CO)(PPh_3)_3$ as the catalyst, deuterium adds to 2-butyne to form only 2,3-dideutero *cis*-butene, and no HD is formed. If H_2/D_2 mixtures are used, the rate of equilibration is faster than addition and the distribution of deuterium in the butene is random (Table 6). Similar results are obtained with $HRh(DBP)_4$ as the catalyst. The rate of H_2/D_2 equilibration using either monohydride complex is not affected appreciably by the butyne.

(b) 2-Butyne/[$RhCl(PPh_3)_3$]. In pure benzene, the formation of monodeutero addition products can be diminished by the addition of perchloric acid or phenols. The report that, in a mixture of the acidic alcohol, trifluoroethanol, and benzene, the hydrogenation of 1-hexyne is faster than in benzene by a factor of 6 led us to hydrogenate 2-butyne in this mixed solvent [22]. The initial hydrogen addition rate increased by a factor of 6.5 over the reaction in benzene (Fig. 2). On the other hand, the rate of the H_2–D_2 equilibration decreased by 60%. Table 5 shows the expected consequence as a lower proportion of *cis*-2-butene-d_1 (5.7% at 85% conversion). Because the fraction of the product, which contains a single deuterium atom, is much greater than

Table 2. Comparison of the initial rates of addition to 2-butyne and norbornene with the competing equilibration of equimolar H_2–D_2 mixtures catalyzed by rhodium complexes in benzene at 15°C*

Complex	Hydrocarbon [S]	Equilibration $10^6 \times R/2$, mol/s	Addition** $10^6 k$ [S], mol/s
1	–	1.25	–
	2-Butyne	1.74	0.30
	Norbornene	0.43	0.58
2	–	3.1	–
	2-Butyne	4.3	0.030
	Norbornene	2.0	4.1
3	–	5.1	–
	2-Butyne	5.9	0.021
	Norbornene	1.69	0.048

* Comparisons of the relative reactivities for a given reaction between different catalysts or different hydrocarbons is qualitative, because the complexes exhibit different relationships between their concentration and the specific reaction rates. The concentration of the complex used in experiments without unsaturated hydrocarbon or with 2-butyne was 3.7×10^{-4} M, and with norbornene, 8.6×10^{-4} M.

** The initial amounts of 2-butyne and norbornene in the system were 0.0106 and 0.0051 mol, respectively.

Table 3. Initial rates of hydrogenations and deuterations catalyzed by rhodium complexes in benzene at 15°C

Complex	Concentration, M	Hydrocarbon	k, $s^{-1} \times 10^5$	
			k_H	k_D
I	9.4×10^{-4}	2-Butyne	0.21	0.27
I	9.4×10^{-4}	Norbornene	11.1	12.3
II	3.7×10^{-4}	2-Butyne	0.32	0.17
II	8.6×10^{-4}	Norbornene	99.0	63.0
III	3.7×10^{-4}	2-Butyne	2.13	1.42
III	8.0×10^{-4}	Norbornene	1.02	0.66

Table 4. Comparison of the initial rates of addition to 2-butyne and 1-hexene with the competing equilibration of equimolar H_2–D_2 mixtures catalyzed by $ClRh(PPh_3)_3$ in the mixed solvent benzene : trifluoroethanol at 15°C*

Hydrocarbon [S]**	Equilibration $10^6 \times R/2$, mol/s	Addition 10^6k [S], mol/s
2-Butyne	***	1.59
2-Butyne	3.63	1.94
2-Butyne****	0.50	3.00
1-Hexene	0.98	12.8
1-Hexene****	0.15	5.4

* $[ClRh(PPh_3)_3]$, 2.2×10^{-3} M in 50 ml benzene : trifluoroethanol 4 : 1 by volume.

** 2-Butyne, 0.011 mol; 1-hexene, 0.036 mol.

*** D_2 only.

**** 0.008 mol of perchloric acid added.

the fraction of HD found in the gas phase at the time of sampling, most of the monodeuterated product appears to be formed by means other than the addition of HD. An alternative conclusion is presented in the Discussion. At 100% conversion, only 1.1% of *cis*-2-butene-d_1 is formed when perchloric acid is added to the solvent mixture. Compared to the result obtained in pure benzene, the hydrogenation rate increased about 10 times and the rate of the H_2–D_2 equilibration was lowered by a factor of 3.

Reaction with 1-hexene. In a direct comparison with the early studies of Osborn, Jardin, Young, and Wilkinson, the effect of the mixed solvent benzene–trifluoroethanol upon the addition of H_2–D_2 mixtures to 1-hexene is shown in Tables 4 and 5 [3]. The rate of forming the saturated product is five times greater than the rate of forming HD, and, accordingly, the fraction of monodeuterohexane is much lower than in benzene (4.6% at 82% conversion of alkene in the mixed solvent compared to 26% at 92% conversion in benzene). The addition of perchloric acid further retards both the rate of the H_2–D_2 equilibration and the addition of H_2/D_2 and results in a higher proportion of hexane-d_1 than that found in the mixed solvent alone (4.3% at 33% conversion, 7.8% at 54% conversion).

Selectivity in the addition of D_2 to alkynes to form *cis*-alkene. To determine the selectivity of the hydrogenation of an alkyne in the mixture of benzene and trifluoroethanol, 2-butyne and the hexynes were deuterated under an atmosphere of deuterium. Hydridotetrakis(triphenylphosphine)rhodium(I) tends to cause olefin isomerization at low hydrogen pressure [4], and if the hydridorhodium complex is involved in this hydrogenation system, the isomerization of the *cis*-alkene, the initial product, will be competitive with addition and give a mixture of alkenes [20]. In the case of 2-butyne, the selectivity of the hydrogenation of alkyne is 100% with no isomerization product. On the other hand, the selectivity in the initial hydrogenation of 1-hexyne, 2-hexyne, and 3-hexyne to their respective *cis*-alkene differs, yielding a maximum of 93, 55, and 53% of the alkene, with a very high proportion of D_2 products in the alkenes and d_4 products in the alkanes (see Table 5), which indicates that the reaction proceeds under these conditions with little reversibility of the process. Also, the product alkenes are not isomerized, which is uncommon in both homogeneous and heterogeneous catalytic hydrogenations.

Norbornene. The high internal strain in norbornene is released in part when it is hydrogenated to norbornane [23]. The rates of hydrogenation of norbornene catalyzed by $ClRh(PPh_3)_3$, $HRh(CO)(PPh_3)_3$, and $HRh(DBP)_4$ are greater than the rate of hydrogenation of 2-butyne. The rate of H_2–D_2 equilibration is depressed in the presence of norbornene, unlike the result with 2-butyne. Table 2 shows that the ratio of the rate of hydrogenation to the rate of the H_2–D_2 equilibration are 1.3, 2.1, and 0.03 in the case of norbornene compared to 0.17, 0.007, and 0.0035 in the case of 2-butyne when catalyzed by $ClRh(PPh_3)_3$, $HRh(CO)(PPh_3)$, and $HRh(DBP)_4$, respectively.

When hydridorhodium complexes are used, the distribution of deuterium in the products is independent of the progress of the reaction, which is consistent with the results for 2-butyne (Tables 6, 7). On the other hand, if the Wilkinson complex is used, the proportion of d_1-product formed increases with the progress of the reaction, which indicates that it is derived at least in part from the addition of HD.

Table 5. Distribution of deuterium in the products of the addition of equimolar mixtures of H_2–D_2 or D_2 to alkynes and alkenes catalyzed by $ClRh(PPh_3)_3$ in benzene–trifluoroethanol (1 : 1) at 15°C*

Unsaturated hydrocarbon	Gas	Conv., %	Products, %					
			HD	d_0	d_1	d_2	d_3	d_4
2-Butyne	D_2	55	<0.1	0.0	1.2	98.8	0.0	0.0
2-Butyne	D_2/H_2	85	1.5	44.6	5.7	46.7	3.0	0.0
2-Butyne**	D_2/H_2	100	<0.1	48.2	1.1	50.7	0.0	0.0
1-Hexene	D_2/H_2	82	4.9	45.8	4.6	49.2	0.0	0.0
1-Hexene**	D_2/H_2	33	1.1	46.0	4.3	49.2	0.4	0.0
1-Hexene***	D_2	88 (ene)	–	0.0	1.6	98.4	0.5	0.0
		12 (ane)	–	0.0	0.0	0.0	2.1	96.4
2-Hexyne***	D_2	51 (*cis*)	–	0.0	1.5	98.5	0.0	0.0
		41 (ane)	–	0.0	0.0	0.0	3.8	96.2
3-Hexyne***	D_2	53 (*cis*)	–	0.0	1.7	98.3	0.0	0.0
		30 (ane)	–	0.0	0.0	0.0	2.3	96.1

* $[ClRh(PPh_3)_3] = 4.8 \times 10^{-3}$ M; [unsatd hydrocarbon] = 0.2 M and 50 ml of solvent mixture.

** 0.008 mol of perchloric acid added.

*** Initial rates relative to 2-butyne are 4.7, 1.3, and 0.6 for 1-, 2-, and 3-hexyne, respectively.

Table 6. A comparison of observed and computed distribution patterns of deuterium in *cis*-2-butene from reductions of 2-butyne with H_2/D_2 in the benzene solution

Catalyst	$HRh(CO)(PPh_3)_3$		$HRh(DBP)_4$		$ClRh(PPh_3)_3$		$ClRh(PPh_3)_3$*	
Conv., %	14		5		28		13	
HD, %	43		40		8		3	
Dist.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.**	Obsd.	Calcd.**
d_0	28.8	29.2	29.2	30.9	27.0	16.7 (10.3)	35.9	7.9 (28.0)
d_1	48.9	49.7	51.1	49.4	38.5	38.5	18.8	18.8
d_2	20.7	21.1	18.2	19.8	34.2	22.2 (12.0)	43.7	11.0 (32.7)
d_3	1.6	–	1.5	–	0.3	–	1.6	–
d_{av}	0.95	0.92	0.92	0.89	1.08	1.07	1.11	1.06
N_2		1.00		1.00		0.78		0.39
N_A		0.0		0.0		0.22		0.61
a/b***		0.85		0.80		1.15		1.18

* 2.2×10^{-3} M PPh_3 added.

** Parenthesis indicates contribution of addition of $H_2(D_2)$.

*** The ratios of addition of D to H. The calculation is based on the ratio sum of d_2 and one-half of d_1 with the sum of d_0 and one-half of d_1.

DISCUSSION

In general, the results of the reaction of H_2–D_2 mixtures with several unsaturated hydrocarbons were, qualitatively, as anticipated. The monohydride complexes catalyze the H_2–D_2 equilibration, and the addition products contain an apparently randomized distribution of the added hydrogen and deuterium. The Wilkinson complex, which represents a dihydride catalyst, yields predominantly addition products containing either two hydrogen atoms or two deuterium atoms per molecule in keeping with the currently accepted mechanism [24] but also produces monodeutero addition products in excess of the average proportion of HD in the gas phase. Solutions of the Wilkinson complex also

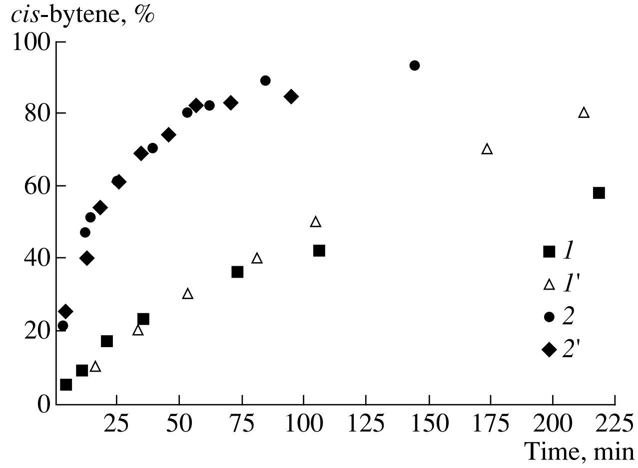


Fig. 2. Formation of *cis*-butene in the deuteration of 2-butyne catalyzed by $ClRh(PPh_3)_3$ in benzene, 0.42 M 2-butyne (*1*), 0.21 M 2-butyne (*1'*); in a mixture of benzene and trifluoroethanol, 0.42 M 2-butyne (*2*), 0.21 M 2-butyne (*2'*).

catalyze the H_2–D_2 equilibration, though much less effectively than the monohydride complexes. This exchange reaction and its relation to the distribution of deuterium in the products is our principal concern.

H_2–D_2 equilibration in solutions of $ClRh(PPh_3)_3$. A plausible explanation for the catalysis of the exchange is that small amounts of a monohydride complex are formed according to Eq. (II) [4, 25]

$$\begin{aligned} &ClRh(PPh_3)_3 + H_2 \rightleftharpoons H_2RhCl(PPh_3)_3 \\ &\quad \rightleftharpoons HRh(PPh_3)_3 + HCl. \end{aligned} \qquad (II)$$

The ratio of phosphine ligand to rhodium affects the rate of equilibration as it does the rate of the hydrogenation of alkenes. Excess ligand slows the reaction by converting the trisphosphine to the tetrakisphosphine complex, which is unable to combine with dihydrogen (Eq. (III)) [20]. The optimum ratio of L/Rh appears to be 3 : 1

$$HRh(PPh3)_3 + PPh_3 \rightleftharpoons HRh(PPh_3)_4 \qquad (III)$$

(Fig. 1), the rate being less at lower ratios presumably because of the formation of the chloro bridging dimmer $[ClRh(PPh_3)_2]_2$ [17]. According to Montelatici *et al.*, hydrogenation is also affected by the L/Rh ratio, but the maximum appears at close to 2 : 1 [26]. The latter result is consistent with the generally accepted mechanism of the $ClRhL_3$ catalyzed hydrogenation of alkenes in which the formation of a complex of the composition $H_2ClRh(PPh_3)_2$ or the reaction of the latter with alkene is rate-controlling [6, 21, 26].

The amount of hydridorhodium complex in the reaction mixture should be affected by acids and bases. Indeed, the H_2–D_2 exchange rate increases with the introduction of small amounts of triethylamine and decreases with the addition of perchloric acid or phenols. The fact that 2,4,5-trichlorophenol depresses the equilibrium rate more than does hydroquinone indicates that the phenols are not acting as free radical inhibitors, hydroquinone being superior to the chlorophenol in this regard.

Catalysis by $ClRh(PPh_3)_3$ in benzene–trifluoroethanol solutions. Trifluoroethanol is a poor solvent for the Wilkinson complex; however, as reported by Candlin and Oldham, the solvent mixture of benzene and tri-

Table 7. A comparison of observed and computed distribution patterns of deuterium in norbornane

Catalyst	$HRh(CO)(PPh_3)_3$*		$HR(DBP)_4$*		$Clh(PPh_3)_3$**		$ClRh(PPh_3)_3$**	
Conv., %	25		22		51		10	
HD, %	0.4		16		2		1	
Dist.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.***	obsd.	calcd.***
d_0	27.7	27.1	24.3	26.3	44.7	2.8 (41.9)	47.2	1.4 (45.8)
d_1	48.8	49.9	51.9	50.0	5.8	5.9	2.8	2.8
d_2	23.5	23.0	23.8	23.7	49.3	3.3 (46.0)	50.0	1.5 (48.5)
d_{av}	0.96	0.96	1.00	0.98	1.0	1.04	1.03	1.03
N_2		1.00		1.00		0.12		0.06
N_A		0.00		0.00		0.88		0.94
a/*b*****		0.92		0.95		1.10		1.10

* Benzene solvent.

** Benzene : trifluoroethanol (4 : 1).

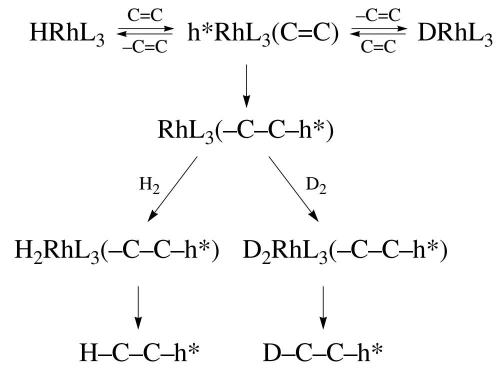
*** Parenthesis indicates contribution of addition of $H_2(D_2)$.

**** The ratios of addition of D to H. The calculation is based on the ratio sum of d_2 and one-half of d_1 with the sum of d_0 and one-half of d_1.

fluoroethanol accelerates the hydrogenation of alkynes but has little effect on the hydrogenation of alkenes [22]. These authors suggested that intramolecular hydrogen bonding between the acidic alcohol and the chloride ligand promoted oxidative addition. A more likely consequence of hydrogen bonding is to stabilize an ion pair, the positive ion being a cationic rhodium complex, which has been shown to be more selective than the Wilkinson catalyst for the hydrogenation of alkynes in the presence of alkenes [28]. That the increase in the rate of hydrogenation is not due to a change in mechanism from one involving a dihydride catalyst to a monohydride, as observed with the cationic complexes described by Schrock and Osborn, is indicated by the molecular identity of H_2 or D_2 in the products of addition: it is improved relative to that observed in the solvent benzene, particularly if a small amount of perchloric acid is added to the mixed solvent. The absence of alkene isomerization is also an indicator of the dominance of the dihydride catalytic mechanism. The rate of the H_2–D_2 equilibration is faster in benzene–trifluoroethanol than in benzene alone, but the increase in the rate does not match the increase in the rate of alkyne hydrogenation. As in benzene, a strong acid lowers the rate of equilibration. The next section examines the information that may be obtained from the distribution of deuterium in the products.

Distribution patterns of added H (D). With $ClRh(PPh_3)_3$ as the catalyst, the distribution of the added H (D) is partly random in the products of the addition of the H_2–D_2 mixtures to the unsaturated hydrocarbons. A random distribution may arise if (1) H (D) is mixed before entering the catalytic cycle of addition as molecular H_2 (D_2 or HD) or (2) if addition proceeds within the catalytic cycle via, for example, $HRh(PPh_3)_3$ as the catalyst (scheme). The proportion of product formed via the first path will depend largely upon the rate of the H_2–D_2 equilibration relative to the rate of addition. The proportion of randomized addition formed via the $HRh(PPh_3)_3$ catalytic cycle will depend upon the amount of the latter complex present and upon the relative reactivity of the unsaturated hydrocarbon towards the competing mechanisms of hydrogenation. The contribution of this latter mechanism to the product should be recognized most readily at low conversions (providing that the H_2–D_2 equilibration is not too rapid relative to addition) and, in principle, its contribution can be estimated through an extrapolation of the results to initial conditions where the partial pressure of HD is zero. In the absence of sufficient data to accomplish this extrapolation, we note that the *cis*-2-butene-d_1 (from 2-butyne) and norbornane-d_1 (from norbornene) are formed in greater amounts than the fraction of HD in the gas phase at the time of sampling (Table 5). The gas phase composition in HD, however, may lag behind the solution composition where HD is produced because of resistance to gas transfer at the gas–liquid interface. Or, perhaps, the exchange involves an interconversion via the monohydride complex (Eq. (IV)) but transfer to an unsaturated hydrocarbon is faster than the loss of dihydrogen (H_2, HD, or D_2):

$$H_2ClRh(PPh_3)_3 + D_2ClRh(PPh_3)_3 \rightleftharpoons 2HDClRh(PPh_3)_3. \tag{IV}$$



h* = H or D

Scheme. Formation of a random distribution of added H(D) to alkene from an H_2/D_2 mixture via catalysis by $HRh(PPh_3)_3$.

Differences in the kinetic isotope effects for the addition of H_2 (D_2) offer a means for deciding amongst some of these possibilities. The kinetic isotope effect (k_H/k_D) for the addition of H_2 (D_2) to 2-butyne, which can be estimated from the results in Table 3, has the values 1.5 and 1.8 for the catalysts $HRh(DBP)_4$ and $HRh(CO)(PPh_3)_3$; for norbornene, the rate ratios are 1.5 and 1.6, respectively, which may be compared with 1.47 reported for the reaction of 1-hexene in benzene catalyzed by $HRh(CO)(PPh_3)_3$ [16]. These differ markedly from the inverse kinetic isotope effect for additions catalyzed by $ClRh(PPh_3)_3$ found here and reported by others. The distribution patterns of added H (D), however, contain information regarding an isotope effect, which may be different from those determined from the rates of addition of H_2 and D_2.

The isotope effect for introducing H (D) to two positions in 2-butyne or norbornene via a randomizing process can be obtained from the distribution of H (D) in the products. Thus, the value of a/b (D/H) in the binomial formula, which reproduces the observed distribution of d_0, d_1, and d_2 and the average deuterium content of the product, is the inverse of the required isotope effect providing that the initial pressures of H_2 and D_2 are equal [10]. Applied to catalysis by the monohydride complexes, the values of 1.05–1.18 are obtained (Tables 6, 7). Clearly, these are smaller than the directly measured kinetic isotope effects of 1.5–1.6, but, unlike the latter, the product distributions are a function of a sequence of hydrogen transfers rather than of a single elementary step.

To evaluate the isotope effect for the formation of the randomized distribution of H (D) in the products when $ClRh(PPh_3)_3$ is used, the observed distribution and the average deuterium content are fitted by a calculation that assumes that a portion of the product (N_A) corresponds to the addition of H_2 or D_2 in the ratio of the directly observed kinetic isotope effect and that the remainder (N_2) corresponds to a binomial distribution with the adjusted parameter (a/b). The calculated value of a/b for the random portion of the addition either to 2-butyne or to norbornene corresponds to a kinetic isotope effect of 0.87–0.90, which indicates that the random addition proceeds via the $ClRh(PPh_3)_3$ cycle rather than via $HRh(PPh_3)_3$ (Tables 6, 7). Apparently, the amount of $HRh(PPh_3)_3$ present in these solutions is too small to affect appreciably the addition of hydrogen (H_2, D_2, HD) to either 1-butyne or norbornene.

Kinetic isotope effects. As indicated above, the hydrogen–deuterium kinetic isotope effects in the formation of the products can be estimated from the product isotopic distributions. For catalysis by $ClRh(PPH_3)_3$, the most direct relationship is probably that between the ratio product-d_0/product-d_2 obtained using 1 : 1 mixtures of H_2 and D_2 and in which the amount of HD formed is minimized [4]. The data in Tables 6 and 7 are relevant and yield an isotope effect of 0.95 for 2-butyne, 0.92 for 1-hexene, and 0.95 for norbornene. The rates differ among these unsaturated compounds in benzene by a factor of 10, and in the solvent mixture benzene–trifluoroethanol the rates are much enhanced. The small isotope effect is consistent with a product controlling transition state in which both bond forming and bond breaking to hydrogen are important [28]. The change in solvent to benzene–trifluoroethanol does not appear to alter the mechanism.

CONCLUSIONS

By a careful analysis of the results, we have shown that the two types of complexes, monohydrido and dihydrido catalysts, are characterized by differences in their ability to catalyze the H_2–D_2 equilibration (the former does, the latter does not) and in the patterns of distribution of added H (D) in the product obtained using mixtures of H_2 and D_2 (the former yields a randomized distribution, and the latter retains the molecular identity of the added H_2 and D_2 in the product). In these real examples, the situations are complicated, because some nominal catalysts consist of more than one type. However, the characteristic reactions of a particular type of catalyst can be revealed by optimizing the conditions.

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