The Pd(II)-catalyzed homogeneous isomerization of hexenes

Darwin B. Dahl, Claire Davies, Robin Hyden [1], Margarita L. Kirova [2], William G. Lloyd *

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101, USA

Abstract

The isomerization of linear hexenes in alcoholic media, catalyzed by low concentrations of $PdCl_2$ in the presence of $CuCl_2$, has been examined. Effects of reagent concentrations, alcohol and temperature are noted. Values of the rate and equilibrium constants for the ten rate-determining steps have been calculated for reactions in methanol at 30°C. The turnover number for the π-complex group is $48,100 \pm 3,800$ h^{-1}. No skeletal isomerization is detected. These isomerizations appear to proceed through π-allylic intermediates. © 1997 Elsevier Science B.V.

Keywords: Homogeneous; Isomerization; Palladium(II); Alkenes; Alcohols

1. Introduction

The oxidation of linear hexenes in methanol, catalyzed by dissolved $PdCl_2$, yields a mixture of hexanones and hexanal, with product composition essentially independent of the starting hexene isomer [1]. 1-octene under similar conditions has previously been found to produce a mixture of the three linear octanones [2–7]. These observations imply the presence of fast alkene isomerization steps which take place prior to oxidation. This paper explores these isomerizations.

2. Results and discussion

At much lower concentrations of [Pd(II)] than used in oxidations, 1-hexene readily isomerizes in alcoholic solution at ambient temperatures (Fig. 1). Oxidation is negligible under these conditions: when 1-hexene has undergone a 20% conversion to internal hexenes, the extent of oxidation is less than 0.005%.

2.1. Effects of some variables

In the absence of $CuCl_2$ or other appropriate reoxidant the Pd(II) species is gradually reduced to Pd(0) by the slow concurrent oxidation–reduction reaction [1,2,8], as is the case for the corresponding Wacker oxidation [9,10]. Other reoxidants, such as benzoquinone [8], $BiCl_3$ [5], air [11], perchloric acid [12] and $FeCl_3$ [13],

* Corresponding author. E-mail: wglloyd@mindspring.com.
[1] Present address: Department of Chemical Engineering, Purdue University, West Lafayette, IN, USA.
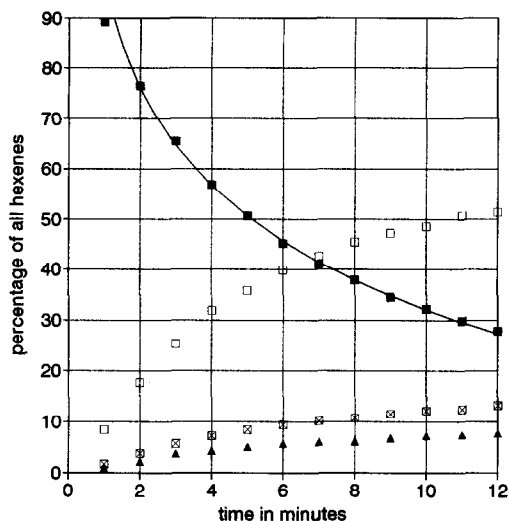[2] Present address: Department of Chemistry, Wayne State University, Detroit, MI, USA.

Fig. 1. Isomerization of 1-hexene in methanol at 25.0°C. Hexene, 0.1951 M; PdCl$_2$, 7.80E − 5 M; CuCl$_2$, 4.88E − 3 M; 25.0°C. (■) 1-hexene, (□) E-2-hexene and Z-3-hexene; (⊠) E-3-hexene, (▲) Z-2-hexene.

have been reported. CuCl$_2$ remains the most widely used reoxidant. Most of the present isomerizations have been conducted with 5E − 6 to 6E − 4 M PdCl$_2$ and 1.0E − 3 M CuCl$_2$.

Hexene isomerizations proceed readily at 25–50°C in light alcohols, and reasonably well with primary alcohols through 1-octanol. Ethanediol, both propanediols and 1,4-butanediol are also effective solvents. 2-(2-methoxy)ethoxyethanol (methyl carbitol®) fails to dissolve the catalyst. 2,2′-oxydiethanol (diethylene glycol) readily dissolves the catalyst but is immiscible with hexene. However, a 1:1 mixture of these two solvents dissolves both catalyst and hexenes, permitting both isomeriza-

tion and, much more slowly, oxidation. Any alcoholic solvent which can provide a homogeneous solution of PdCl$_2$, CuCl$_2$ and hexene apparently will function as a solvent medium for these isomerizations. Reactions are fast in methanol and ethanol and are significantly slower in higher alcohols.

All five linear hexenes are isomerized, as seen in Table 1. 1-hexene is markedly more reactive than the internal hexenes.

As the starting concentration of 1-hexene is increased from 0.0727 to 0.364 M the overall isomerization rate increases in a smooth convex-upwards curve, ultimately limited by the catalyst concentration (fixed here at 2.00E − 5 M). A reciprocal plot of rate v. concentration (Fig. 2) is substantially linear, implying a first-order dependence upon [1-hexene].

With 1-hexene at 0.1454 M and CuCl$_2$ at 1.00E − 3 M in methanol at 30°C, PdCl$_2$ concentration was varied, in a series of runs, from 0 to 5.00E − 4 M. Isomerization rate is 0 in the absence of Pd(II) and varies linearly with [Pd(II)]. Fig. 3 shows this relationship and also a parallel series with Z-2-hexene.

The effect of varying concentrations of CuCl$_2$ upon 1-hexene isomerization in methanol at 30°C is shown in Fig. 4 (solid squares). These runs were carried out with 1-hexene 0.1454 M and PdCl$_2$ at 2.00E − 5 M. At CuCl$_2$ concentrations below 1.00E − 4 M the reoxidation reaction probably cannot keep up with the slow concurrent Pd(II) reduction (hexene oxidation). There is a flat optimum concentration range of

Table 1
Typical isomerization rates of linear hexenes in methanol at 30°C

Isomer	Conc. (mol l^{-1})	[PdCl$_2$] (mol l^{-1})	[CuCl$_2$] (mol l^{-1})	Initial rate, (mol l^{-1} min^{-1})	Relative reactivity [a] (l mol^{-1} min^{-1})
1-hexene	0.1455	2.00E − 5	1.00E − 3	6.55E − 3	2300
E-2-hexene	0.1609	2.00E − 4	1.00E − 3	1.16E − 3	36
Z-2-hexene	0.1484	2.00E − 4	1.00E − 3	2.07E − 3	70
E-3-hexene	0.1706	6.00E − 4	1.00E − 3	3.58E − 3	35
Z-3-hexene	0.1550	6.00E − 4	1.00E − 3	2.55E − 3	27

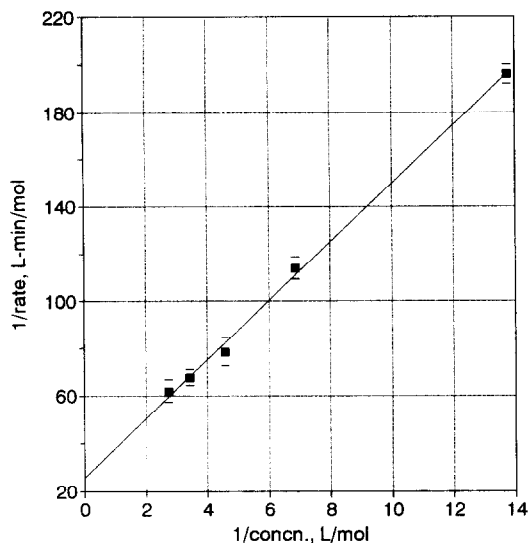[a] Relative reactivity = (initial rate)/([hexene] × [PdCl$_2$]).

Fig. 2. Effect of 1-hexene concentration upon rate at 30.0°C. $PdCl_2$, 2.00E − 5 M; $CuCl_2$, 1.00E − 3 M in methanol. Intercept 25.7 (± 3.2) l min mol^{-1}.

Fig. 4. Effect of $CuCl_2$ concentration upon isomerization rates of 1-hexene and Z-2-hexene in two alcohols. (■) 1-hexene 0.1454 M, $PdCl_2$ 2.00E − 5 M in methanol at 30.0°C; (▲) 1-hexene 0.1951 M $PdCl_2$ 9.76E − 4 M in 1-butanol at 25.0°C.

3E − 4 M to 3E − 3 M $CuCl_2$. At higher copper chloride concentrations the isomerization rate is retarded.

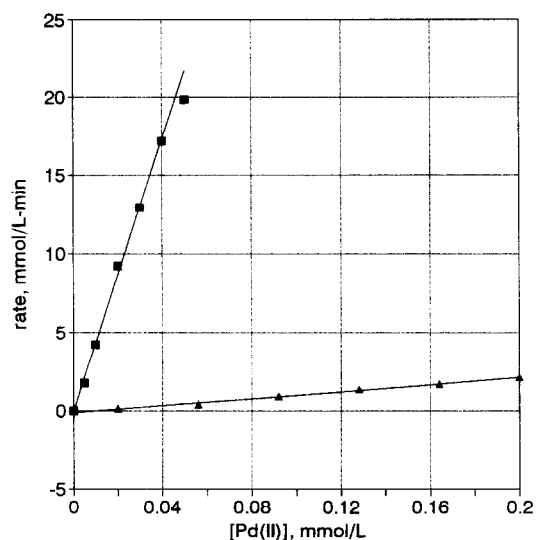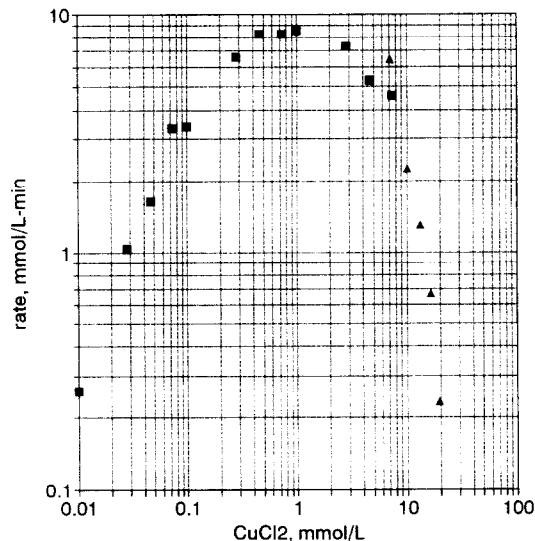This trend is continued by data obtained with 1-hexene at an initial concentration of 0.1951 M

Fig. 3. Effect of $PdCl_2$ concentration upon isomerization rates of 1-hexene and Z-2-hexene at 30.0°C. (■) 1-hexene 0.1454 M with $CuCl_2$ 1.00E − 3 M; (▲) Z-2-hexene 0.1484 M with $CuCl_2$ 1.00E − 3 M.

and $PdCl_2$ 9.76E − 5 M in 1-butanol at 25°C (solid triangles in Fig. 4). Here the $CuCl_2$ concentration was varied from 7.0E − 3 to 1.96E − 2 M, all of these concentrations being well above optimum for these isomerizations.

The addition of small amounts of LiCl to otherwise balanced catalyst systems sharply retards isomerization. In one pair of experiments 1-hexene was isomerized in 1-butanol at 25°C with $PdCl_2$ 9.75E − 4 M and $CuCl_2$ 3.907E − 3 M. The addition of LiCl 7.79E − 3 M reduced the 20 min conversion from 75.6 to 2.1%.

This rate suppression by excess chloride ion is not surprising. The kinetics of chloride ion inhibition of Wacker oxidations has been thoroughly studied [4,9,10,14–18] and critically reviewed [11,17]. This retardation applies as well to methanolic systems [19,20]. On the other hand, some chloride (or halide) ion is required to solubilize $PdCl_2$, in methanol as in water.

The effect of temperature upon the isomerization rate has been studied in both methanol and butanol. 1-hexene 0.1454 M was examined in methanol with 2.00E − 5 M $PdCl_2$ and 1.00E − 3 M $CuCl_2$ at 18–38°C. The Arrhenius plot of
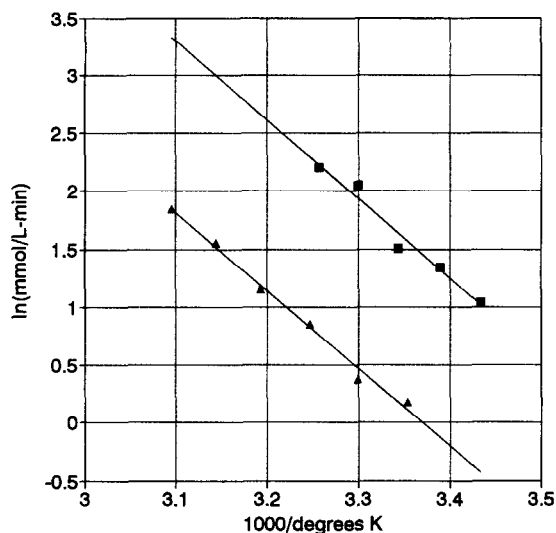
Fig. 5. Arrhenius plots of 1-hexene isomerization in two alcohols. (■) 1-Hexene 0.1454 M, PdCl$_2$ 2.00E−5 M, CuCl$_2$ 1.00E−3 M in methanol; (▲) 1-hexene 0.1950 M, PdCl$_2$ 9.76E−4 M, CuCl$_2$ 1.015E−2 M in 1-butanol.

the initial isomerization rates is shown in Fig. 5 (solid squares). A similar series was run in 1-butanol, with hexene 0.1950 M, PdCl$_2$ 9.76E −4 M and CuCl$_2$ 1.015E − 2 M, at 15–50°C (Fig. 5, solid triangles). The parallel slopes of each data set imply that the same chemical processes are rate-limiting over these temperature ranges. The least-squares activation energies are 56 ± 6 kJ for the methanol series, 55.7 ± 2.5 kJ for the butanol series.

2.2. Estimation of rate constants

The pattern of possible reactions among five linear hexene isomers, five π-complexes and a number of intermediate species (ion pairs or organopalladium compounds) is daunting. We make a major simplifying assumption: The rates of interconversion among π-complexes are fast in comparison with the rates of π-complex formation and dissociation.

An experimental basis for this assumption is seen upon examination of the product formation curves from the isomerizations of 1- and 3-hexenes. In Fig. 1, for example, E-3-hexene is

immediately formed as 1-hexene commences to isomerize and the rate of formation of E-3-hexene is at its maximum at this initial moment. Similarly, the isomerization of E-3-hexene immediately produces 1-hexene, even at very low E-3-hexene conversions. A process requiring the intermediation of 2-hexenes would present very different formation curves.

The pool of interconverting π-complexes can therefore be viewed as a single supercomplex, here designated as Π. For the following discussion Pd = uncomplexed palladium, Pd° = total palladium, k_A is the rate constant of the reaction of isomer H$_A$ with Pd to give Π and k'_A is the dissociation rate constant of Π to give H$_A$.

It is further assumed that [Π] rapidly achieves steady-state concentration early in the isomerization. When the starting isomer H$_A$ is virtually the only isomer present, this condition requires that

$$k_A[\text{Pd}][\text{H}_A] = [\Pi] \times \sum k' \qquad (1)$$

where $\sum k'$ is the sum of all π-complex dissociation constants. Substituting ([Pd°] − [Π]) for [Pd] and rearranging,

$$[\Pi] = \frac{k_A[\text{Pd}°][\text{H}_A]}{k_A[\text{H}_A] + \sum k'} \qquad (2)$$

Taking the general relationship:

$$-\text{d}[\text{H}_A]/\text{d}t = k_A[\text{Pd}][\text{H}_A] - k'_A[\Pi] \qquad (3)$$

and substituting for [Pd] as above,

$$-\text{d}[\text{H}_A]/\text{d}t = k_A[\text{Pd}°][\text{H}_A] \\ - [\Pi](k_A[\text{H}_A] + k'_A) \qquad (4)$$

Substituting for [Π] by Eq. (2),

$$-\text{d}[\text{H}_A]/\text{d}t \\ = \frac{k_A[\text{Pd}°][\text{H}_A] \times (\sum k' - k'_A)}{k_A[\text{H}_A] + \sum k'} \qquad (5)$$

When H$_A$ is 1-hexene, which is only about 1% of the equilibrium isomer mixture, we make the

additional assumption, to be tested later, that $k'_A \ll \Sigma k'$; then Eq. (5) for the case of 1-hexene may be closely approximated by:

$$-d[H_{1H}]/dt \approx \frac{k_{1H}[Pd^\circ][H_{1H}] \times \Sigma k'}{k_{1H}[H_{1H}] + \Sigma k'} \qquad (6)$$

When both sides of Eq. (6) are inverted,

$$\frac{1}{-d[H_{1H}]/dt} \approx \frac{1}{[Pd^\circ] \times \Sigma k'}$$

$$+ \frac{1}{k_{1H}[Pd^\circ][H_{1H}]} \qquad (7)$$

Eq. (7) is linear for $1/[H_{1H}]$ versus $1/\text{rate}$, with the first term on the right hand side being the intercept term. As has been seen (Fig. 2), this relationship is linear for 1-hexene, and consequently the intercept in Fig. 2 yields a first approximation of $\Sigma k'$.

2.3. Calculation A

A crude starting assumption is taken, that $[Pd] = [\Pi] = \frac{1}{2}[Pd^\circ]$. Pooling nine isomerizations of 1-hexene at 30°C we then calculate k_{1H} from Eq. (2). Using this average value to revise $[\Pi]$ for each run, k_{1H} is recalculated, then $[\Pi]$ is revised again, continuing through ten iterations. Estimates of k_{1H} converge rapidly: for the last three iterations they are 5875, 5872 and 5871 1 mol^{-1} min^{-1}, std. dev. $\pm$ 306, for 1-hexene isomerizations under these conditions.

From the initial rates of formation of each product (experimentally determined) we obtain estimates of k'_B, k'_C, ... using the final estimates of $[\Pi]$ for each run along with the empirical relationship:

$$d[H_B]/dt_{\text{initial}} = k'_B[\Pi] \qquad (8)$$

The remaining constants, k_B, k_C, ... are similarly estimated by parallel analysis of isomerization runs of E-2-hexene, Z-2-hexene and E-3-hexene. This exercise provides a set of first estimates of the rate constants in this system.

2.4. Calculation B

A second series of calculations commences with these estimates. First, Eq. (4) is rearranged:

$$[\Pi] = \frac{k_A[Pd^\circ][H_A] + d[H_A]/dt}{k_A[H_A] + k'_A} \qquad (9)$$

Then, taking k_{1H} and k'_{1H} from the previous calculations, $[\Pi]$ for each run is reestimated by Eq. (9). As before, k'_{E2}, k'_{Z2} and k'_{E3} are estimated from the product formation curves. The value of k_{E2} is estimated from isomerizations of E-2-hexene. This same procedure is carried out for the other isomers, to provide a second set of better rate constants and a better estimate of $\Sigma k'$ than that taken from the intercept of Fig. 2. When this entire series of calculations is repeated a rapid convergence of values is obtained (Table 2). Fig. 6 shows the observed isomer concentrations in run No. 1 along with the calculated isomer concentration curves, using the values of Table 2 and a 2 ms calculational mesh.

A key assumption in the foregoing is that $[\Pi]$ rapidly attains a steady-state concentration, long before substantial isomerization has occurred. This is now testable. When the kinetically determined rate constants of Table 2 are used to generate concentration curves of [Pd(II)] and $[\Pi]$, the curves reach constant concentrations in well under 1 s. A second assumption, that $k'_{1\text{-hexene}} \ll \Sigma k'$, is also shown to be reason-

Table 2

Estimates of kinetic rate constants [a]

	k_{1H}	k'_{1H}	k_{E2}	k'_{E2}	k_{Z2}	k'_{Z2}	k_{E3}	k'_{E3}	k_{Z3}	k'_{Z3}
Calc. A, iter. 10	5871	60.3	44.7	576	59.1	92.0	37.1	146	28.0	4.0
Calc. B, iter. 1	6590	51.2	133.0	564	67.7	90.0	45.7	143	29.3	4.0
Calc. B, iter. 2	6470	51.1	133.0	563	67.7	89.9	45.7	143	29.3	4.0
Calc. B, iter. 3	6475	51.1	133.0	563	67.7	89.9	45.7	143	29.3	4.0

[a] Dimensions of k_{1H}, k_{E2}, k_{Z2}, k_{E3}, k_{Z3}: l mol^{-1} min^{-1}; dimensions of k'_{1H}, k'_{E2}, k'_{Z2}, k'_{E3}, k'_{Z3}: min^{-1}.

able. Fig. 7 shows typical curves for initial concentrations of 1-hexene 0.100 M and $PdCl_2$ 2.00E − 5 M, using the constants of Table 2 and a 1 ms calculational mesh.

The equilibrium distribution of linear hexenes is readily calculable from ΔG_f° data. We have also determined this experimentally, using both the capillary-SIM analysis and capillary analysis of the dibromo derivatives [21]. Results are given in Table 3. There are distinct differences in isomer distribution between ideal values and the Pd(II)-methanol system values. In this isomerization system the E-isomers are favored over the corresponding Z-isomers. Furthermore, 1-hexene, although still a minor component at equilibrium, is more abundant in this system than is predicted from the thermodynamic data.

When the estimated rate constants of Table 2 are accommodated to the equilibrium requirements of the system (Table 3), most kinetic values require only minor adjustments ($\sim 10\%$ relative) to conform to thermodynamic requirements. There is, however, one glaring discrepancy: if the kinetic-based value for k'_{1H} is accepted, then the equilibrium data require a value
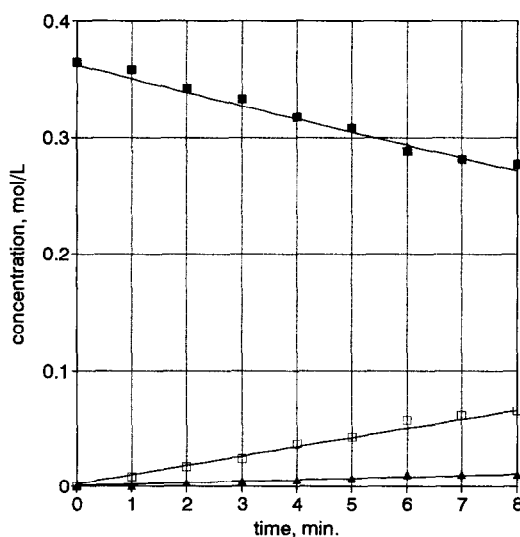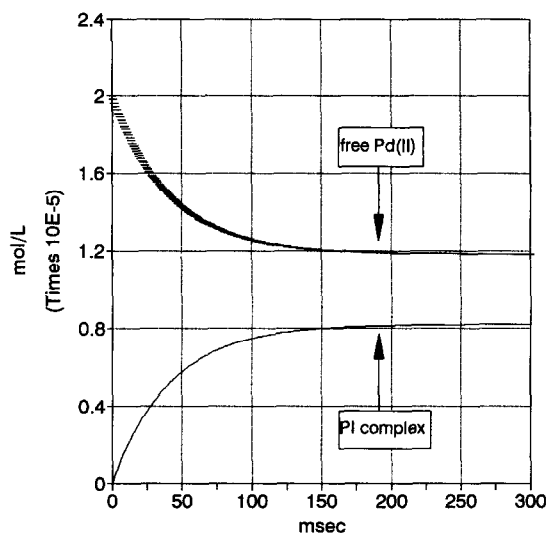
Fig. 7. Concentrations of uncomplexed [Pd(II)] and of [Π] during the first 300 milliseconds of reaction. Calculations use the final constants of Table 2 and assumed starting concentrations of 0.100 M 1-hexene and 3.00E − 5 M $PdCl_2$. Calculational mesh is 1 ms.

for k_{1H} which is an order of magnitude lower than that found from kinetic measurements. This anomaly is discussed below.

A common measure of catalyst activity is turnover number (TN), the number of molecules of reactant converted per atom or molecule of catalyst per unit time.

$$TN = \frac{mol\ l^{-1}\ h^{-1}\ reacted}{mol\ l^{-1}\ of\ catalyst} \qquad (10)$$

TN can be calculated on the basis of total catalyst present (total $PdCl_2$), or on the basis of the concentration of the active species, in this system, [Π]. Table 4 presents calculations for nine isomerization runs with 1-hexene. On the basis of the nominal (total $PdCl_2$) concentrations, TN = 30,100 ± 5,270 h^{-1} (relative error 17.5%). On the basis of the concentrations of the active π-complexes ([Π]), TN = 48,100 ± 3,820 h^{-1} (relative error 7.9%). When the starting 1-hexene concentrations differ substantially, for example, in runs 4 through 7, the nominal TN changes in concert with hexene concentration. The TN calculated from the active catalyst (Π) concentration remains essentially constant. The Π-based calculation is the more useful.

Fig. 6. Conformity of the kinetic rate constants of Table 2 to the experimental data of Run 1. (■) 1-hexene, (□) E-2-hexene, (▲) Z-2-hexene.

Table 3
Equilibrium distribution of linear hexene isomers

1-hexene (%)	E-2-hexene (%)	Z-2-hexene (%)	E-3-hexene (%)	Z-3-hexene (%)	Source
0.42	36.2	38.9	21.9	2.6	ideal gas [a]
0.29	36.5	38.9	22.0	2.3	liquid [b]
1.19 ± 0.24	61.4 ± 2.2	16.6 ± 1.1	19.8 ± 1.6	1.0 ± 0.04	this work
Rate constants					
550.0	117	64.3	56.2	29.3	k, adjusted [c]
51.1	631	94.4	110.0	2.8	k', adjusted [c]
Equilibrium constants [d]					
10.8	0.185	0.68	0.51	10.5	$K = k/k'$

[a] At 25°C, calculated from Ref. [33].
[b] At 25°C, calculated from Ref. [34].
[c] k in l mol^{-1} min^{-1} and k' in min^{-1}, adjusted from Table 2 data, to conform within 1 standard deviation to the equilibrium values found in the PdCl$_2$–CuCl$_2$–methanol system.
[d] K in l mol^{-1}. K_{1H} ($= k_{1H}/k'_{1H}$) falls from 127 (pure 1-hexene) to 10.8 l mol^{-1} (equilibrium mixture).

Raw TN estimates from isomerizations of other hexenes are somewhat smaller: 40,100, 38,400 and 17,600 h^{-1} for Z-2-hexene, E-3-hexene and E-2-hexene, respectively. When these estimates are corrected for the reverse reactions (most notably for E-2-hexene, which makes up 61% of equilibrium mixtures), the agreement is fairly good. Dividing each of these estimates by the fraction of [Π] which goes to form other isomers, the adjusted TN's are ~ 48,100, ~ 47,900 and ~ 45,600 h^{-1}, respectively.

2.5. Indicators of mechanism

The acid-catalyzed rearrangement of neohexene has been known for many decades [22]. Under acidic conditions (trifluoroacetic acid in methanol at 55°C) 3,3-dimethyl-1-butene (neohexene) undergoes the expected carbocation

Table 4
Calculated values of [Π] and turnover number [a]

Run	[1-hexene]°	[Pd°] (mol l^{-1})	[Π] (mol l^{-1})	%[Pd°] as [Π]	Nominal (TN, h^{-1})	Active cat. [b] (TN, h^{-1})
1	0.1454	5.00E − 5	2.74E − 5	55	23,800	43,400
2	0.1454	4.00E − 5	2.06E − 5	52	25,800	49,900
3	0.1454	3.00E − 5	1.54E − 5	51	25,900	50,300
4	0.1454	1.00E − 5	5.23E − 6	52	25,400	48,500
5	0.364	2.00E − 5	1.48E − 5	74	34,800	47,200
6	0.291	2.00E − 5	1.38E − 5	69	32,700	47,300
7	0.218	2.00E − 5	1.31E − 5	66	27,100	41,300
8	0.360	1.98E − 5	1.40E − 5	71	39,000	55,300
9	0.363	2.00E − 5	1.46E − 5	73	36,000	49,400
Average					30,100	48,100
Std. dev.					5,270	3,820
Rel. error					17.5%	7.9%

[a] In methanol, with CuCl$_2$ 1.00E − 3 M, 30°C, using values of k_{1H} and k'_{1H} from Table 2. [Π] is calculated by Eq. (9). Turnover number (TN) is calculated by Eq. (10).
[b] Based upon the total concentration of π-complexed palladium(II).

rearrangement to (mostly) 2,3-dimethyl-1-butene. With methanolic $PdCl_2$–$CuCl_2$ there is no detectable skeletal rearrangement. However, the addition of neohexene retards the isomerization of 1-hexene. At 30°C and in the presence of $2.00E - 5$ M $PdCl_2$ and $1.00E - 3$ M $CuCl_2$ the initial isomerization rate of 0.1212 M 1-hexene is reduced from 7.25 to 1.33 mmol l^{-1} min^{-1} by the addition of 0.0762 M neohexene. 1-hexene isomerization is also retarded by the addition of internal linear hexenes. Addition of 0.124 M E-2-hexene reduces the 1-hexene isomerization rate from 7.25 to 4.06 mmol l^{-1} min^{-1}. This suggests an explanation for the disparity in estimates of k_{1H} in Tables 2 and 3. At near-equilibrium conditions the ratio of internal hexenes to 1-hexene approaches 100:1. Under these conditions much of the Pd(II) is associated with internal hexenes and the apparent value of k_{1H} is depressed.

When Pd(0) 5% on $- 100$ mesh charcoal powder is added to a methanolic solution of 1-hexene (0.0987 M) and the mixture stirred at 25°C there is no detectable isomerization in 10 min and less than 0.2% isomerization in 120 min. A parallel run with $PdCl_2$ and $CuCl_2$ underwent a 77% isomerization in 10 min. Pd(0), as Maitlis has noted [23], fails to catalyze alkene isomerization.

Two major mechanisms have been proposed to account for olefin isomerizations [23,24]: al-lylic hydride abstraction by Pd to form a π-allylic intermediate [7,25–28] and a hydridopalladium addition–elimination sequence [29,30]. Each of these appears to be operative under certain experimental conditions. The following results bear upon the question of which mechanism may be applicable to the present data.

Methanol ($\varepsilon = 32.6$, $\Delta H_v \approx 970$ J cm^{-3}) and 1-butanol ($\varepsilon = 17.1$, $\Delta H_v \approx 620$ J cm^{-3}) differ substantially in polarity. The isomerization rates in methanol (Fig. 5) are 5- to 6-fold greater than those in 1-butanol. Furthermore, the catalyst concentration in butanol is 49-fold greater than that in the methanol runs. Thus there is a considerable difference in reactivity in these two alcohols. Yet the activation energies of 1-hexene isomerization are identical within experimental error. Also in both alcohols the formation rates of E- and Z-2-hexene are uniform and in substantially the same proportions. Specifically, there is no tendency in either system for the Z-isomer to predominate at low conversions. Some other isomerizations believed to proceed by π-allylic intermediates have been reported to be characterized by high initial Z/E ratios [24,30].

A series of test isomerizations was made with methylpentenes and dimethylbutenes at ambient temperature. The results are summarized in Table 5. Several conclusions are indicated. (a) Isomerization from an open position in the chain

Table 5
Isomerization products of branched hexenes [a]

Reactant	Time [b] (da)	2m1p (%)	3m1p (%)	4m1p (%)	s2m2p (%)	E3m2p (%)	Z3m2p (%)	E4m2p (%)	Z4m2p (%)	2e1b (%)	23m1b (%)	33m1b (%)	23m2b (%)
3m1p	1	-	[38]	-	-	34	19	-	-	9	-	-	-
Z4m2p	1	13	-	0.7	60	-	-	23	[4]	-	-	-	-
2m2p	1	11	-	-	[83]	-	-	5	1	-	-	-	-
Z3m2p	1	-	-	-	-	4	[94]	-	-	1	-	-	-
2m1p	3	[65]	-	0.3	30	-	-	3	0.6	-	-	-	-
23m1b	3	-	-	-	-	-	-	-	-	-	[99]	-	1
33m1b	1	-	-	-	-	-	-	-	-	-	-	[100]	-
23m2b	3	-	-	-	-	-	-	-	-	-	-	-	[100]

[a] Abbreviations: b = butene; p = pentene; m = methyl; e = ethyl. Thus, Z4m2p = Z-4-methyl-2-pentene.
[b] 2.5% v/v hexene in methanol containing $PdCl_2$ $2.20E - 4$ M, $CuCl_2$ $1.10E - 3$ M, at 27–28°C.

to a branch point (e.g. 4-methyl-2-pentene to 2-methyl-2-pentene) is fast as well as thermodynamically favored. (b) Isomerization from a branch point to an open position in the chain (e.g. 2-methyl-2-pentene to 4-methyl-2-pentene), disfavoured thermodynamically, proceeds to low conversions. (c) Isomerization through a branch point (e.g. 2-methyl-1-pentene to 2-methyl-2-pentene) is slower, even when thermodynamically favored (in this instance by 6.4 kJ). (d) Isomerization to a tetrasubstituted ethylene is very slow and isomerization of a tetrasubstituted ethylene does not occur detectably under these conditions. (e) The E-isomer in all cases is favored over the corresponding Z-isomer.

When 1-hexene is isomerized by a solution of $PdCl_2$ and $CuCl_2$ in methanol-d_4 at ambient temperature, the reaction proceeds similarly to that in undeuterated methanol. Deuteride extraction might be expected to show a primary kinetic isotope effect; none was observed. If the hydrido ligand of the Pd ion is obtained from the alcohol solvent, as is generally assumed for the addition–elimination mechanism, E-2-hexene and other product isomers formed from the reaction in CD_3OD solution might be expected to have acquired at least one deuterium atom. Following this isomerization to near-equilibrium, we found no detectable D uptake, based upon the relative intensities of the m/e 85 $(m + 1)^+$ and 84 $(m)^+$ ions: the mass ratio is a constant 0.066, characteristic of undeuterated hexenes. The least squares slope for the change in this ratio with time is $-1.60E - 4\%$ min^{-1}, std. dev. $\pm 1.26E - 3\%$ min^{-1}, that is, zero slope with time. This was confirmed by examining the intensities of the strong methyl escape peak $(m/e$ 69) and m/e 70. These observations argue against the addition-elimination mechanism for isomerizations under these conditions and hence tend to support the π-allylic mechanism.

The π-allylic cationic intermediate has two 'axial' bonds, at Z-1 and Z-3. The separation of these bonds is very close to that of the axial bonds in cyclohexanes. Intermediates leading to

the formation of E-isomers can have hydrogen atoms at each of these sites. Intermediates leading to the formation of Z-isomers must have at least one of these sites occupied by an alkyl group:
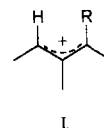
The 1,3-nonbonding interaction disfavours these Z-isomer precursors, especially the Z-3-hexene precursor for which $R = C_2H_5$. These considerations are reflected in the high pseudo-equilibrium concentrations of 1-hexene and E-2-hexene and the low pseudo-equilibrium concentrations of Z-2- and Z-3-hexene in the $PdCl_2$-methanol system, relative to thermodynamic equilibria (Table 3).

Tang and Sherrington have recently reported on 1-octene and 1-decene isomerizations catalyzed by Pd(II) supported on benzimidazole polymers dispersed in ethanol containing $CuCl_2$ reoxidant [7]. Their turnover number for 1-decene at 50°C is 228 h^{-1}. In the present system, with a mobile and homogeneously dispersed Pd(II) catalyst, the turnover number at 30°C (Table 4) is ~ 48,000 h^{-1}.

It has been generally recognized that terminal alkenes react more rapidly than internal alkenes. The quantitative estimates (Table 2) show that, for linear hexenes in methanol:

· 1-hexene is initially nearly 50-fold more reactive than E-2-hexene.

· E-hexenes exhibit about twice the reactivity of the corresponding Z-isomers.

· 3-hexenes exhibit about one third the reactivity of the corresponding (E- or Z-)2-hexenes.

· The rates of formation of the several hexene isomers from the Π-complex pool fall in the order E-2 $\gg$ E-3 > Z-2 > 1- $\gg$ Z-3.

From the great facility of these Pd(II)-catalyzed isomerizations at ambient temperatures it seems likely that there is no additional charge

separation required in forming the π-allylic cation. This suggests that the active free Pd(II) species may carry a single positive charge, $ClPdL_3^+$.

3. Experimental

All chemicals are reagent grade. Catalyst solutions were prepared by weighing the solid salts with a plastic-clad spatula into weighing flasks, transferring quantitatively to a clean dry volumetric flask, adding alcohol solvent and stirring overnight. Solutions were then brought to volume by addition of fresh solvent. These solutions are concentrates, typically $PdCl_2$ 0.0220–0.1100 M and $CuCl_2$ 0.1100–0.5500 M and are then diluted as needed for the isomerization runs. Hexene solutions were prepared volumetrically: 5.00_0 ml of 1-hexene into a total volume of 25 ml alcohol provides a concentrate of 1.599 M 1-hexene.

Methanolic ammonia was made up of three volumes of reagent methanol and one volume of concentrated aqueous ammonia. A set of septum-capped 2 ml vials was prepared by adding 0.10 ml of the methanolic ammonia solution to each vial, then stoppering.

For a typical kinetic run, a 25 ml flask containing a small teflon-clad stirbar was immersed to its neck in a constant-temperature waterbath. A charge of 10 ml of catalyst solution was added, the flask corked, and the flask contents allowed to come to temperature. The isomerization reaction was commenced by adding 1.00_0 ml of the desired hexene solution and mixing vigorously for 10 s. At a series of selected times, a 1 ml portion of the reaction mixture was withdrawn and transferred to a labelled vial. Methanolic ammonia arrests the isomerization by converting both Pd(II) and Cu(II) ions into catalytically inactive $M(NH_3)_4^{2+}$ species. Vials were then stored under refrigeration until analyzed.

Vial contents were analyzed using a Shi-madzu QP-5000 GC/mass spectrometer fitted with a 60 m × 0.32 mm bonded dimethylsiloxane phase, at 35°C and 1.5 ml/min He carrier. After initial identification of all isomers by their mass spectra, runs with linear hexenes were made in the selected ion monitoring mode (m/e 41, 42, 55, 56), which with this system provides threshold sensitivity of < 10 pg on-column. Response factors for each of the linear hexenes were determined by replicate analyses of standards.

The Z-3-hexene peak is small at equilibrium in these systems and is flanked closely by the larger E-3 and E-2 isomer peaks [31,32]. Even under optimized capillary chromatographic conditions the Z-3 peak emerges fused to the tail of the E-3 peak. This analytical problem has been solved by converting the mixtures of hexene isomers to the corresponding vic-dibromohexanes by a stereospecific anti-bromination, as described elsewhere [21].

The deuterium isotope experiment with 1-hexene was carried out by adding the alkene to a solution of 2.20E − 4 M $PdCl_2$ and 1.10E − 3 M $CuCl_2$ in methanol-d_4 (Aldrich Chemical, 99.9 + % D), allowing the mixture to stand for 135 min and withdrawing portions periodically for gc/ms analysis.

References

[1] M.L. Kirova, D.B. Dahl, W.G. Lloyd, J. Mol. Catal. 88 (1994) 301.
[2] W.G. Lloyd, B.J. Luberoff, J. Org. Chem. 34 (1969) 3949.
[3] M. Kolb, E. Bratz, K. Dialer, J. Mol. Catal. 2 (1977) 399.
[4] A. Kaszonyi, J. Vojtko, M. Hrušovský, Collect. Czech. Chem. Commun. (1982) 2128.
[5] J.-M. Brégault, M. Faraj, J. Martin, C. Martin, N. J. Chem. 11 (1987) 337.
[6] D.C. Sherrington, H.-G. Tang, Proc. 5th Int. Symp. on Macromolecule-Metal Complexes, 1993, p. 193 (publ. 1994).
[7] H.-G. Tang, D.C. Sherrington, J. Mol. Catal. 94 (1994) 7.
[8] I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Dokl. Akad. Nauk SSSR 133 (1960) 377.
[9] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, Angew. Chem. 71 (1959) 176.
[10] I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Dokl. Akad. Nauk SSSR 130 (1960) 821.

[11] P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel, Dordrecht, 1980, p. 42.

[12] J.E. Backvall, R.B. Hopkins, M. Grennberg, M.M. Mader, A.K. Awasthi, J. Am. Chem. Soc. 112 (1990) 5160.

[13] R. Jira, W. Freiesleben, Organometal. React. 3 (1972) 1.

[14] W. Hafner, R. Jira, J. Sedlmeier, J. Smidt, Chem. Ber. 95 (1962) 1575.

[15] I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Dokl. Akad. Nauk SSSR 152 (1963) 147.

[16] I.I. Moiseev, O.G. Levanda, M.N. Vargaftik, J. Am. Chem. Soc. 96 (1974) 1003.

[17] P.M. Henry, J. Am. Chem. Soc. 86 (1964) 3246.

[18] P.M. Henry, Accts. Chem. Res. (1973) 16.

[19] P. François, Ann. Chim. Paris 4 (14) (1969) 371.

[20] H.-B. Lee, P.M. Henry, Can. J. Chem. 54 (1976) 1726.

[21] D.B. Dahl, C. Davies, W.G. Lloyd, Microchem. J. (1997), submitted.

[22] A. Gillet, Bull. Soc. Chim. Belg. 29 (1920) 192.

[23] P.M. Maitlis, The Organic Chemistry of Palladium, vol. 2, Academic Press, NY, 1971, pp. 128–139.

[24] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley-Interscience, New York, 1992, pp. 11–16.

[25] F.F. Howard, A.J. Chalk, J. Am. Chem. Soc. 88 (1966) 3491.

[26] R. Hüttel, M. McNiff, Chem. Ber. 106 (1973) 1789.

[27] B.M. Trost, P.E. Streghe, Tetrahedron Lett. (1974) 2603.

[28] B.M. Trost, Tetrahedron 33 (1977) 2615.

[29] R. Cramer, R.V. Lindsay, J. Am. Chem. Soc. 88 (1966) 3534.

[30] D. Pauley, F. Anderson, T. Hudlicky, Org. Synth. 67 (1989) 121.

[31] C.-F. Chien, D.L. Furio, M.M. Kopecni, R.J. Laub, J. High Res. Chrom. Chrom. Commun. 6 (1983) 577.

[32] A.J. Lubeck, D.L. Sutton, J. High Res. Chrom. Chrom. Commun. 7 (1984) 542.

[33] D.R. Stull, E.F. Westrum, Jr., G.C. Sinke, The Chemical Thermodyanmics of Organic Compounds, Wiley, New York, 1969.

[34] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.