Dihydride Transfer. A Bimolecular Mechanism in the Isomerization of 
cis-Dihydrobromo(carbonyl)(bis)(diphenylphosphino)ethane)iridium, 
$\text{IrH}_2\text{Br(CO)(dppe)}$ 
by 
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INTRODUCTION

The oxidative addition of H₂ to a metal complex has been extensively studied over the past 20 years because of its relevance to H₂ activation in homogeneous hydrogenation and hydroformylation.1,2 One of the most thoroughly investigated systems in this context is Vasta's complex, trans-[Ir(H)(CO)(PCy3)] (11, which reacts with H₂ according to eqn (1).3 Based on kinetic and mechanistic studies,3,4 H₂ oxidative addition is generally viewed as a concerted process with a triangular H₂ transition state leading to a cis dihydride product.

Abstract: The oxidative addition of H₂ to Ir(III)(CO)(dppe), 2, to give 1,2-bis(cyclohexadienylphosphine)iridium, (H₂Ir(III)(CO)(dppe)) has been extensively studied over the past 20 years because of its relevance to H₂ activation in homogeneous hydrogenation and hydroformylation.1,2 One of the most thoroughly investigated systems in this context is Vasta's complex, trans-[Ir(H)(CO)(PCy3)] (11, which reacts with H₂ according to eqn (1).3 Based on kinetic and mechanistic studies,3,4 H₂ oxidative addition is generally viewed as a concerted process with a triangular H₂ transition state leading to a cis dihydride product.

Recently we began investigating the oxidative addition chemistry of the related set of cis phosphine complexes Ir(III)(CO)(dppe), 2, and have discovered that its concerted oxidative addition reactions proceed under kinetic control.3,5 With complexes 2, the oxidative addition of H₂ can follow two possible pathways, 4 and 5, as shown in eqn (2), leading to different diastereomers, 3 and 6, respectively, for the concerted process. Pathway 4 corresponds to H₂ approach to the square planar complex with the molecular axis of H₂ parallel to P-Ir-CO as shown in A. The concerted oxidative addition along 4 takes place with a bending of the trans P-Ir-CO axis so that one hydride of the product becomes trans to CO and the other trans to P. Pathway 5 corresponds to approach with the H₂ molecular axis parallel to P-Ir-CO.
The isomerization of the kinetic isomer 3 to the thermodynamic isomer 4 for 3 : Br was also examined by us in detail. 64 Based on the observation that 3 rapidly forms 3 CH when placed under H2, it was determined that the initial oxidative addition is rapid and reversible, occurring much faster than isomerization. The isomerization in acetone under H2 follows clean first order kinetics with an observed rate constant, k_{obs}, at 55 °C of 1.85 x 10^{-1} sec^{-1}, corresponding to a half-life of 63 minutes. At 55 °C the half-life of the kinetic isomer 3 is about 35 hours. Two possible mechanisms for isomerization appeared consistent with the kinetic data. The first was an intramolecular rearrangement, while the second corresponds to a reductive elimination-oxidative addition sequence with the formation of 2 as an intermediate. We favored this latter pathway: \[ 3 \rightarrow 2 + H_2 \rightarrow 4 \] reductively to 3 occurs much more rapidly than isomerization.

The clean first order kinetics for the isomerization, however, were observed only in acetone solvent, and under an excess of hydrogen. When the reaction was studied in benzene, the isomerization proceeded much more rapidly with an apparent half-life of ca. 3 hours at 55 °C, although the kinetics were not found to be reproducible. The isomerization of 3 to 4 was also found to be inhibited by TFOH and accelerated by added AgH2 in benzene and by added H2 in acetone. Perhaps most disturbing was the observation that isomerization could proceed more rapidly in rigorously degummed acetone when less H2 was present. Since the proposed reductive elimination-oxidative addition sequence for isomerization possessed no kinetic dependence on H2, our observation suggested that another mechanism for isomerization existed. We therefore reinvestigated the isomerization of the kinetic isomer 3 to the thermodynamic isomer 4 as a function of H2 pressure.

In this paper we describe in detail that investigation, including the observation that a second isomerization mechanism involving hydrogen transfer between metal centers competes with the first order isomerization mechanism at
ambient temperature, and as the rate mechanism operating at temperatures below 10 °C.

Experimental Section

All kinetic experiments were carried out in resealable 5 mm NMR tubes fitted with a Teflon valve purchased from Trilium Glass. H₂ was used as received (Air Products C.P., 99.9%). Acetone-d₂ (Aldrich Gold label) was distilled from 4A molecular sieves. "H NMR spectra were recorded on a Bruker WM-400 spectrometer at 400 MHz. The temperature of the probe was regulated with a Bruker B-71-1000 temperature control unit.

The complex [Ir(III)Cl(DCIP)] was synthesized following the procedure previously reported. 80

General Procedure for Sample Preparation. A stock solution of [Ir(III)Cl(DCIP)] (9.55 x 10⁻³ M, 0.02 g of complex in 3 mL solvent) was prepared in acetone-d₂ and stored under H₂ in a dry box. For each experiment, 0.50 ± 0.02 mL of the stock solution was transferred to the NMR tube which was then connected to a high vacuum line containing an H₂ inlet. After three freeze-pump-thaw cycles, the solution was maintained at 0 °C in an ice bath while the sample was placed under the desired pressure of H₂ by opening the valve at the top of the NMR tube. The sample was then shaken thoroughly to ensure mixing of H₂, and placed in the thermostated probe of the NMR spectrometer. The total volume of the NMR tube was determined to be 2.00 ± 0.05 mL with a solution volume for each run of 0.50 ± 0.05 mL.

RESULTS AND DISCUSSION

The kinetics of the isomerization reaction of the cis dihydride of formula Ir₂H₂[Br(DCIP)] has been studied over a wide range of H₂ pressures, from 12 mm to 610 mm of added H₂. The reactions were monitored by ¹H NMR spectroscopy, using the integrals of the hydride resonances of isomers 3 and 4 to determine the relative amounts of each isomer present. Through comparison of the integral of the entire hydride region to the integral of the entire methylene region, the amount of unreacted Ir₂(H₂)(DCIP) was determined for each NMR tube experiment. 0.5 mL of a 5.55 x 10⁻³ M stock solution of Ir₂(H₂)(DCIP), prepared and stored under nitrogen, was used.

Isomerization under 610 mm H₂ Pressure. The kinetic results of the isomerization of 3 to 4 under 610 mm of added H₂ reveal that the reaction proceeds by a clean first-order process. At 28 °C, the half-life for isomerization is 10 hours, and the corresponding k₉₂ is 3.65 x 10⁻³ min⁻¹. A plot of ln (3) vs. time is linear, as shown in Figure 1, essentially confirming the earlier results of Johnson and Eisenberg. 68

As discussed in the Introduction, the isomerization mechanism favored by us previously was a reductive elimination/oxidative addition sequence shown as eqn (3) based on the fact that the initial oxidative addition was found to be fast and irreversible. The rate law for this mechanism, given as eqn (6), depends only on the concentration of the kinetic dithiane 3 and shows no dependence on hydrogen pressure. Since the initial oxidative addition is highly stereo-selective, k₁₂ is much greater than k₂ and the rate law (6) corresponds to that of a simple pseudo-first-order.

\[
\frac{d(3)}{dt} = k_{12}(3) - k_{21}(3) - k_{22}(3) = \frac{k_{12}(3)}{k_{21}} \frac{[3]}{[2]}\]
The reaction of isomerization for three experimental runs under 200, 300, and 400 mm of added H₂ were found to be approximately first order. That is, plots of ln (1-x) vs. time are linear for at least two half lives, although they show a slight deviation from linearity at early reaction times. This deviation is most evident at the lowest of these pressures of H₂ as shown in Figure 2. A more significant, and initially more puzzling, aspect of the kinetic runs under these pressures was that the rate of isomerization was observed to be faster as the pressure of added H₂ was lowered, as shown in Table 3. This variation in rate with H₂ pressure was inconsistent with the reductive elimination/oxidative addition sequence of (3) and its rate law, (4), which shows no H₂ dependence. A plot of k₁ vs. 1/[H₂] suggested that a second isomerization pathway was operating in addition to (3), while showing that the inverse dependence of (1) for this pathway was not strictly linear.

Isomerization under low pressures of hydrogen. Four experimental runs were carried out under 12, 22, 29, and 41 mm of added H₂, all of which correspond to amounts of added hydrogen less than one equivalent of starting complex, IrBr(CO)(dppe). These reactions proceeded much more quickly than those under higher pressures of H₂—typically, isomerizations were complete in less than 15 hours. Attempts were made to fit the data to a first order equation, but plots of ln (1-x) vs. time showed significant deviations from linearity. Clearly, the isomerization pathway which was predominant at low pressures of H₂ did not follow first order kinetics.

A second order treatment of this experimental data was more successful in that plots of ln1/[IrI] vs. time were linear, with 1/[IrI] representing the sum of unreacted and unisomerized iridium complexes, 2 = 3. A plot of this data for the run under 22 mm of added H₂ is shown in Figure 3. Contrary to expectations, the data in Table 2 show that the observed second order rate constant, k₂ = 1/[IrI] decreased with decreasing H₂, but a plot of k₂ vs. [H₂] was found to be distinctly nonlinear. Surprisingly, a linear correlation was obtained when a plot of k₂ vs. 1/[H₂] was constructed as shown in Figure 4. The origin of this linear dependence on 1/[H₂] will become apparent below.

We thus conclude that an isomerization mechanism which is second order in complex predominates under low pressures of H₂ and possesses an inverse [H₂] dependence.

Mechanism for the second order isomerization pathway. Under conditions in which less than one equivalent of H₂ is added to the reaction system, both IrBr(CO)(dppe) and the kinetic isomer of IrBr(CO)(dppe), 3, are present in observable concentrations. We propose a bimolecular mechanism involving these two species to explain the isomerization process under these conditions. This mechanism, which is consistent with the kinetic data, involves hydride transfer between Ir species via a biradical intermediate, 5, as shown in eqn. (5):

![Chemical structure diagram](image-url)
The proposal of a dihydropyridine-bridged dinuclear intermediate has precedents in other, closely related studies. In the investigation of the stereoselective oxidative addition of H₂ to various tris[1] complexes of type 2, Johnson and Eisenburg described chemistry involving the reactive intermediate (IrH(CO)PpH₂) generated by benzylic oxidation of (IrH(CO)PpH₂). 4 When the reaction was carried out using the base DBU (1,8-diazabicyclo-(5.4.0)undec-7-ene) under H₂, the products were the tricyclic IrH(CO)PpH₂, 6, and the kinetic dihydropyridine 3, as shown in eqn (1). Use of D₂ showed that whereas most of 6 formed by the oxidative addition of H₂ (or D₂) to IrH(CO)PpH₂, an amount roughly equivalent to the amount of H₂ was produced via a different pathway. Since the thermodynamic dihydropyridine 4 does not reductively eliminate H₂ on the time scale of the experiment, the formation of IrH(CO)PpH₂ which gives 3-D₂ upon reaction with D₂ was proposed to occur by direct dihydropyridine transfer from IrH(CO)PpH₂ to IrH(CO)PpH₂ through a bridged intermediate with concomitant formation of IrH₂(CO)PpH₂.

In an earlier report, Brown and Harrod5 proposed a dihydropyridine-bridged dimer structure in their attempts to convert the monodentate phosphate complex IrH₂(CO)P(C₆H₅)₂PPh₂, 3, to the unsaturated complex IrH₂(CO)P(C₆H₅)₂PPh₂, 4 when the tricyclic 3 was placed under a stream of nitrogen to displace H₂. Subsequent evidence revealed the occurrence of an equilibrium proposed to involve 9 as shown in eqn (1).

Recently, Jones and Negroni described the direct intermolecular transfer of H₂ between a rhodium complex and IrH(CO)PpH₂. 6 Treatment of (κ³-C₅H₄(NO)₂PPh₂)₂Rh, with 1 equivalent of IrH(CO)PpH₂, 2, resulted in the formation of (κ³-C₅H₄(NO)₂PPh₂)₂Rh and the thermodynamically more stable dimer of IrH(CO)PpH₂, 4, as shown in eqn (1). 6 This reaction has proceeded by elimination of H₂ from 10 followed by H₂ oxidative addition to 2, the thermodynamic isomer 3 would have been formed. A control experiment ruled out this possibility, and the results thus strongly support the notion that the reaction between 10 and 2 goes via a dihydropyridine-bridged dinuclear intermediate.
isomerization mechanism shown above in eqn (14) is derived as follows beginning with (14):

rate via bimolecular path = \( \frac{k_3[H_2]}{2} \) \( \text{moles} \)/liter-sec

the concentrations of 2 and 3 are related by an equilibrium constant
expression where \([H_2]\) corresponds to the concentration of dissolved \(H_2\)

Therefore,

\[
\frac{[S]}{[2][H_2]} = \frac{1}{k} = K_{eq}
\]

and

\[
[S] = K_{eq}[2][H_2]
\]

Substituting for (3) into eqn (9) yields (12):

rate via bimolecular path = \( k_3[H_2]^2 \)

we next express the rate in terms of [H2] corresponding to the sum of
unreacted and isomerized \( \text{H}_2 \) species. \( \text{eqn (12)} + \text{eqn (3)}:

\[
[S] = (2 + 3) \times (1 + [H_2])
\]

\[
[S] = (2) \times \frac{1}{1 + [H_2]}
\]

Upon substitution of this expression for \([S]\) into eqn (12) we obtain:

rate via bimolecular path = \( \frac{k_3[H_2]^2}{1 + [H_2]} \)

The \([H_2]\) dependence in rate expression (13) is complex, but it is evident
that the value of \(k_3[H_2]^2\) determines the observed hydrogen dependence of the
'second order' or bimolecular pathway. Two limiting regimes can be envisioned,
which are as follows:

1) For \([H_2] \gg k_3[H_2]^2\), the bimolecular rate \( \propto k_3[H_2]^2\)

2) For \([H_2] \ll k_3[H_2]^2\), the bimolecular rate \( \propto k_3[H_2]^2\)

In this limit, the hydrogen concentration is extremely low, and the rate is propor-

tional to \([H_2]\)

The fact that the observed second order rate constant for isomerization
shows an inverse \([H_2]\) dependence, as illustrated by the data in Table 2, and
the plot in Figure 1, indicates that even at the low \(H_2\) pressures used in the
present isomerization study, \(k_3[H_2]^2\) \(\ll\)

Isomerization under an Intermediate Pressure of \(H_2\)

To examine the isomerization in between the high and low \(H_2\) pressure regimes, an experiment
was carried out under 120 mm of added \(H_2\). Based on IR and Raman spectroscopy, the
kinetic diagram 3 and dissolved \(H_2\), this initial pressure of \(H_2\) corresponds to
0.03 equivalents of \(H_2\) in solution. As in the high \(H_2\) pressure regime, no
\(2[BiBr(COD)dppe]\) is observed in solution. The reaction is near complete in 23 hours,
and surprisingly the best fit of the kinetic data is obtained when the
reaction is treated as a second order, bimolecular process. That is, a
reasonable straight line results from a plot of \([S]\) vs. time. Figure 5,
where \([S]\) in this case represents the concentration of the isomeric
\(2[BiBr(COD)dppe]\).

The Complete Rate Law

The kinetic results described above indicate that both isomerization mechanisms operate to differing extents over the range of \(H_2\) pressures examined. The system with parallel reaction paths, the complete rate expression is given by the sum of the component rate
laws. For the isomerization \(2[BiBr(COD)dppe]\), the complete rate expression
is given by eqn (18) in which there are terms to account for both the first
and second order components. If eqn (18) is correct, then it should be
possible to fit the experimental data to this equation.
In order to analyze the kinetic data in terms of initial rate values, we will give a rate value in $\text{M} \cdot \text{s}^{-1}$ for each run, obtained by assuming initial values of $H_2$ uniformly in the first order or second order reaction. The initial rate was the value of $\text{d}[	ext{H}_2]\text{d}t$ corresponding to $t = 0$ for each run above $0.1 \times 10^{-8} \text{ M}$, whereas the kinetic rate constant, $k_{\text{c}}$, is measured throughout the course of each run. Initial rates for all reactions were determined by fitting the experimental data to Eq. 2, using the method of least squares to a third-order polynomial and extrapolating to $t = 0$. This allows us to ignore the concentration of the thermodynamic upper limit, $H_2$, as seen in Table 3. The initial rate first increases with increasing $[	ext{H}_2]$ and then turns over, decreasing as $[	ext{H}_2]$ continues to increase. This is consistent with the functional dependence of $k_{\text{c}}$ as in Eq. 10, and its two limiting cases described as... 

The concentration of $H_2$ in solution, $[\text{H}_2]$, for each experiment was calculated using the material balance expression, Eq. 11, where $P_{\text{H}_2}(\text{aq})$ is the initial added pressure of $H_2$ in atmospheres, $V_{\text{aq}}$ is the volume above the solution in the NMR tube ($5 \times 10^{-2} \text{ M}$, and $V_{\text{sol}}$ is the solution volume ($0.5 \text{ mL}$).

$$\frac{P_{\text{H}_2} \cdot V_{\text{aq}}}{V_{\text{sol}}} = \frac{[\text{H}_2]}{0.5} \quad (11)$$

The total amount of added hydrogen, $P_{\text{H}_2}(\text{aq}) \cdot V_{\text{aq}}$, is distributed as the amount in solution, $[\text{H}_2]$, the amount above the solution, $P_{\text{H}_2}(\text{g}) \cdot V_{\text{aq}}$, and the amount which is consumed to make products, $[\text{H}_2]$$_{\text{prod}}$. Substitution at $t = 0$ gives using a modified form of Henry's law $[\text{H}_2] = P_{\text{H}_2}(\text{g}) \cdot V_{\text{aq}}$, and for $t > 0$ solving the equilibrium of Eq. 10.

$$\text{Reduced rate} = \text{observed initial rate} - \frac{k_{\text{c}} \cdot [\text{H}_2]}{k_{\text{obs}} \cdot ([\text{H}_2] + [\text{H}_2]_{\text{prod}})^2} \quad (12)$$

A plot of reduced rate vs. $[\text{H}_2] + [\text{H}_2]_{\text{prod}}$ should give a straight line with a slope $= -k_{\text{obs}}/[4k_{\text{c}}]$. As shown in Figure 6, the experimental data fit the derived function reasonably well with two clusters of data points corresponding to the two pressure regimes studied, one with more than 1 equivalent of added $H_2$ and the other with less than 1 equivalent. The fit of the line indicates that the derived equation accurately describes the behavior of the system. The data which are plotted, as well as values for $P_{\text{H}_2}(\text{g})$, $k_{\text{c}}$, and $k_{\text{obs}}$, are given in Table 3.

The very small values for the reduced rate at high $[\text{H}_2]$ indicate little contribution from the second order pathway. From runs at the highest added $H_2$ pressure, we estimate that $k_{\text{obs}}$ is approximately $k_{\text{c}}/k_{\text{H}_2}$ and has a value of $3 \times$...
Different values of the equilibrium constant, $K_{eq}$, were employed in plotting the data with the best fit and error bars obtained using $2 \times 10^3$ m$^{-1}$. Based on this value and the fact that the slope of the line in Fig. 6 is $\epsilon \gamma/2 \nu_0$, we estimate the bimolecular rate constant for isomerization, $k_2$, to be $0.03$ m$^{-1}$ s$^{-1}$.

The temperature dependence of the bimolecular reaction. Further confirmation of the bimolecular mechanism for isomerization was demonstrated by a low-temperature experiment which showed that in the $H_2$ deficient regime isomerization of $\text{MeH}_2\text{C(OH)}$ does not occur. In one experiment, a sample of the kinetic isomer 1 was prepared by addition of $100$ mm of $H_2$ to $\text{MeH}_2\text{C(OH)}$ and kept below $-50 \degree C$ to prevent it from isomerizing. The ethyl $H_2$ was removed by two freeze-pump-thaw cycles, and $200$ mm of $D_2$ was added. After storing the sample to ensure mixing of $D_2$, the tube was maintained at $-23 \degree C$ for 24 hours. A $^{1}H$ NMR spectrum was taken at $-23 \degree C$. This confirmed that no isomerization of $\text{MeH}_2\text{C(OH)}$ occurs at $-23 \degree C$ over a 24 hour period. Another $^{1}H$ NMR sample was prepared by adding $25$ mm of $H_2$ to $\text{MeH}_2\text{C(OH)}$ and kept below $-50 \degree C$ for 24 hours. A $^{1}H$ NMR spectrum revealed that isomerization had occurred to the extent of $31\%$. This experiment thus confirmed that isomerization of 1 to 2 can occur independent of the bimolecular elimination of hydrogen from $\text{MeH}_2\text{C(OH)}$ by a bimolecular path.

Stereochemistry of Allylidyne Transfer. In light of the stereoselective kinetically controlled addition of $H_2$ to $\text{MeH}_2\text{C(OH)}$ to give the kinetic isomer 3, it is interesting to consider why the allylidyne transfer produces the thermodynamic isomer 4. That is, why does allylidyne transfer to 3 proceed with opposite stereoselectivity to that of $H_2$ addition? The answer must be electronic in nature since steric factors for the formation of the two isomers of $\text{MeH}_2\text{C(OH)}$ allylidyne transfer are similar.

In $H_2$ oxidative addition, there are two principal interactions between the $\text{MeH}_2\text{C(OH)}$ complex and the $H_2$ molecule. The first involves a donation from the $\sigma^*$ orbital of $H_2$ to the metal $d^0$ orbital of $\text{MeH}_2\text{C(OH)}$. This interaction is weak, however, and the second is a back-bonding interaction in which electron density is transferred from the metal metal $d_σ$ orbital into the $\sigma^*$ orbital of $H_2$. In addition to this weak interaction, a repulsive $d_π$ interaction between the filled metal $d_π$ orbital and the $H_2$ orbital has been invoked as a major contributor to the activation barrier of the $H_2$ oxidative addition process.

The stereoselectivity of $H_2$ oxidative addition to 3 arises by a preferred binding of one set of trans ligands to 2 which becomes cis to each other and trans to the allylidyne ligands in the product, as shown in A. This preference is expected to be the result of the contribution of the ethylidyne ligands to the transition state and the bending ligands and $H_2$ to the bending ligands and $H_2$, making the barrier approximately $2 \pi$.
repulsive interaction does not exist, and the principal reason for addition along the P-3p(C) axis is removed. In fact, the better d$_4$ donor orbital to iodine(111) apex is the one directed in the plane defined by P-3p(3r) and the 2 axis, and it is in this plane that dihydride transfer occurs. While a detailed theoretical analysis of dihydride transfer remains to be done, we envision that the major orbital interaction takes place between a filled d$_y$ orbital of FeII and the eighth function of H$_2$ possessing the same symmetry.

Conclusions

The kinetic studies which we have described involving the isomerization of the dihydrides of FeH$_2$-Ge(111) show that the reaction proceeds via two different mechanisms. Both mechanisms operate to differing extents throughout the range of H$_2$ concentrations examined, but the limiting regimes may be defined as greater than and less than one equivalent of H$_2$ relative to the unsaturated starting complex, FeH$_2$-Ge(111).

In the presence of excess added hydrogen, the isomerization of 3 to 4 occurs primarily by the first order reductive elimination process. The rate law for this mechanism shows no dependence on H$_2$. However, the half-life for isomerization in this regime ($k_1$H$_2$) at 200 mT decreases with decreasing H$_2$, indicating that the other mechanism which is H$_2$ dependent also operates under these conditions.

The reaction path which predominates under hydrogen deficient conditions involves a direct dihydride transfer through a binuclear dihydride-bridged species. This pathway is dependent on H$_2$, is second order with respect to complex, and follows the rate law shown in eqn (13).

Through the use of initial rates, the kinetic data have been accommodated into a single rate expression having first and second order components. The fit of the data to eqn (120) yields an experimental value for the second order.
### Table 1

<table>
<thead>
<tr>
<th>Initial Conc.</th>
<th>Second Order</th>
<th>Rate Constant, $k$, min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.0</td>
<td>0.74</td>
</tr>
<tr>
<td>400</td>
<td>1.75</td>
<td>0.45</td>
</tr>
<tr>
<td>600</td>
<td>1.40</td>
<td>0.20</td>
</tr>
<tr>
<td>800</td>
<td>1.20</td>
<td>0.10</td>
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</tbody>
</table>

*Calculated from $k_{obs} = 1.55 \times 10^{-4}$, where $k_{obs}$ and $V_{obs}$ are the observed kinetic concentrations for the gas and solution phases, respectively, of the isomer $x$. $k_{obs}$ is the rate constant of the reaction between complex and solution.*

### Table 2

<table>
<thead>
<tr>
<th>Initial Conc.</th>
<th>Second Order</th>
<th>Rate Constant, $k$, min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>20</td>
<td>0.41</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>0.36</td>
<td>0.26</td>
</tr>
<tr>
<td>40</td>
<td>0.32</td>
<td>0.22</td>
</tr>
</tbody>
</table>

*Based on the measured concentrations of $m$, and total isomer species as described in the text. The value shown is given by the expression $k_{obs} = 1.55 \times 10^{-4}$, where $k_{obs}$ and $V_{obs}$ are the observed kinetic concentrations for the gas and solution phases, respectively, of the isomer $x$. $k_{obs}$ is the rate constant of the reaction between complex and solution.*
TABLE 2

Initial rate data for the polymerization of 2 to 4 for All P$_2$H$_6$ pressures.

<table>
<thead>
<tr>
<th>P$_2$H$_6$ (torr)</th>
<th>Up$^a$/cavit</th>
<th>Down$^a$/cavit</th>
<th>Up$^b$/cavit</th>
<th>Down$^b$/cavit</th>
<th>Initial rate</th>
<th>Reduced rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.84</td>
<td>0.1</td>
<td>1.40</td>
<td>0.01</td>
<td>45.4</td>
<td>238.0</td>
</tr>
<tr>
<td>200</td>
<td>4.46</td>
<td>0.2</td>
<td>3.43</td>
<td>0.03</td>
<td>35.4</td>
<td>340.0</td>
</tr>
<tr>
<td>400</td>
<td>8.42</td>
<td>0.3</td>
<td>7.40</td>
<td>0.04</td>
<td>30.3</td>
<td>240.0</td>
</tr>
<tr>
<td>600</td>
<td>16.1</td>
<td>0.6</td>
<td>15.1</td>
<td>0.15</td>
<td>20.5</td>
<td>250.0</td>
</tr>
<tr>
<td>800</td>
<td>32.0</td>
<td>1.2</td>
<td>30.0</td>
<td>0.30</td>
<td>10.5</td>
<td>40.0</td>
</tr>
<tr>
<td>1000</td>
<td>40.0</td>
<td>1.4</td>
<td>38.0</td>
<td>0.40</td>
<td>8.0</td>
<td>50.0</td>
</tr>
<tr>
<td>1200</td>
<td>48.0</td>
<td>1.5</td>
<td>46.0</td>
<td>0.50</td>
<td>6.0</td>
<td>50.0</td>
</tr>
<tr>
<td>1400</td>
<td>56.0</td>
<td>1.6</td>
<td>54.0</td>
<td>0.60</td>
<td>5.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Figure 1: First order plot for the polymerization of 3 to 4 for All P$_2$H$_6$ pressures under 670 torr of added P$_2$.
Figure 2: First order plot for the isomerization of trimethylolpropane under 100 torr added H₂.

Figure 3: Second order plot, \( \frac{d[\text{P}]}{dt} \) vs. time, for the isomerization of trimethylolpropane under 100 torr added H₂.
Figure 4. Plot of the observed second order rate constant, $k_{obs}$, vs. time, for the polymerization of [4-hydroxycyclohexene oxide] with less than 10 equivalents of HCl.

Figure 5. Second order plot, $1/[P]_0$ vs. time, for the polymerization of [4-hydroxycyclohexene oxide] under 1.0 M HCl at $70^\circ$C.
Figure 6: Plot of the reduced rate defined in eqn (10) vs. the function describing the high dependence in the complete rate law.