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MECHANISM OF THE PHOTOCHEMICAL DEHYDROGENATION AND TRANSFER-DEHYDROGENATION OF ALKANES CATALYZED BY *trans*-$Rh(PMe_3)_2(CO)Cl$

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ABSTRACT

$Rh(PMe_3)_2(CO)Cl$ catalyzes the photochemical dehydrogenation of alkanes to yield alkenes. H_2 is evolved or, in the presence of potential hydrogen acceptors such as t–butylethylene and styrene, hydrogen can be transferred to the olefins. The photokinetics and selectivity of the dehydrogenation reactions have been investigated. Both reactions proceed via a single photochemical step, photoextrusion of carbon monoxide from $Rh(PMe_3)_2(CO)Cl$. Study of the transfer-dehydrogenation, particularly of the product ratio (H_2 : hydrogenated acceptor), reveals aspects of the dehydrogenation mechanism including steps subsequent to the turnover-limiting step.

INTRODUCTION

The selective and catalytic functionalization of alkanes has long been recognized as one of the most important and challenging goals in coordination chemistry.[1] In the past decade numerous examples of reactions of alkanes with low-valent transition metal complexes have been discovered, but there have been relatively few examples of derivatizations *catalyzed* by such complexes.[2-6] Recently, Tanaka reported[7] the development of a photochemical rhodium system, related to Eisenberg's benzene carbonylation systems,[8] which effects the terminal carbonylation of *n*–pentane with moderate efficiency.

$$CO + n\text{-}C_5H_{12} \xrightarrow{Rh(PMe_3)_2(CO)Cl \quad h\nu} n\text{-}C_5H_{11}CHO \qquad (1)$$

In addition to the importance of carbonylation, our interest in this system was spurred by the observation that reaction 1 probably involves a 16-electron rhodium alkyl hydride intermediate.[7-10] Such species may be expected to display other forms of catalytic reactivity, which have not been observed with the more familiar 18-electron alkyl hydride insertion products. We have therefore begun a systematic study of the alkane chemistry of *trans*-$RhP_2(CO)Cl$ (**1**, P = PMe_3) and its derivatives. In the course of this study we have found two closely related, highly efficient alkane photoreactions, dehydrogenation[11,12] and transfer-dehydrogenation.[13]

$$\text{alkane} \xrightarrow{\mathbf{1} \quad h\nu} \text{alkene} + H_2 \qquad (2)$$

$$\text{alkane} + RHC{=}CH_2 \xrightarrow{\mathbf{1} \quad h\nu} \text{alkene} + RH_2C\text{-}CH_3 \qquad (3)$$

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Reaction 2 has since been independently reported elsewhere.[14] In this paper we discuss the mechanisms of reactions 2 and 3. In particular we identify the photochemical step necessary to drive the thermodynamically unfavorable[15] reaction 2, which is also the photochemical step of reaction 3.

PHOTODEHYDROGENATION

General features of reaction 2 and *trans*-$RhP_2(CO)Cl$

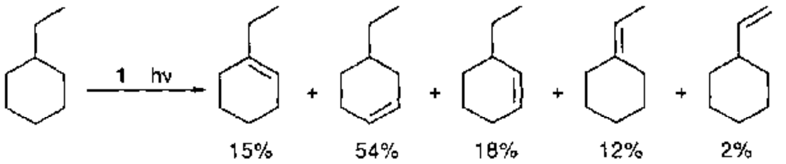
The catalytic system in eq 2 is quite efficient, chemically and photochemically. The quantum yield of reaction 2 for cyclooctane or cyclohexane in the absence of CO atmosphere is 0.097 at 50 °C; at 135 °C the quantum yield is 0.28 (cyclooctane). Total turnover numbers up to 5000, and 72% conversion to cyclooctene have been achieved.

Complex **1** is an air-sensitive, pale yellow compound which is thermally stable in alkane solutions at 135° C. The lowest energy electronic absorption appears at 360 nm ($\varepsilon = 4500\ M^{-1}\ cm^{-1}$). An analogous absorption exhibited by homologous phosphine analogues has been assigned to a $d_{z^2} \rightarrow b_{1\pi}$ transition (MLCT).[16] No change in the ^1H NMR or electronic spectra is observed under an atmosphere of carbon monoxide or an atmosphere of dihydrogen. In the presence of less than ca. one equivalent of trimethylphosphine, exchange of free and coordinated phosphine is rapid on the NMR time scale. The addition of ethylene, cyclooctene, cyclohexene, or trimethylphosphine (up to one equivalent) has no effect on the electronic or infrared spectrum of **1**.

Intramolecular selectivity

The regioselectivity of reaction 2 is unusual in view of the close relationship it bears to transfer-dehydrogenation catalysts and the photodehydrogenation system reported by Crabtree.[5] Those systems display a preference for dehydrogenations involving primary C-H bonds. This is considered to be a reflection of the selectivity (thermodynamic, and in some cases kinetic) shown by transition metal complexes in the stoichiometric insertion into C-H bonds: 1°>2°>>3°.[1, 17]

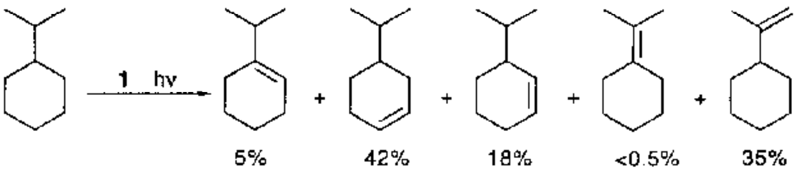
We have examined the intramolecular selectivity of reaction 2 for several cycloalkanes. For example, irradiation of **1** (2.0 mM) in an ethylcyclohexane solution affords the distribution of alkenes shown in eq 4.



(4)

The observed product distribution was time-independent. Control experiments demonstrate that the observed C_8H_{14} isomer distribution is under kinetic control. The low rate of vinylcyclohexane formation demonstrates that steric factors are not dominant in determining the selectivity of **1**, in contrast with previously reported dehydrogenation systems.

The dehydrogenation of isopropylcyclohexane affords the following kinetic distribution of isopropylcyclohexene isomers (eq 5).



(5)

Note that the formation of the disubstituted terminal olefin is much more favorable than formation of the monosubstituted analogue from ethylcyclohexane. This underscores the importance of electronic versus steric factors; in general we observe a trend toward formation of more substituted (more thermodynamically stable) olefins. However, a complete lack of isopropylidenecyclohexane formation is seen in eq 5. The formation of a tetrasubstituted olefin like isopropylidenecyclohexane, *via* a ß-elimination step, would require a tertiary alkyl hydride intermediate. There are no precedents for the oxidative addition of a typical[17d] tertiary C-H bond to a metal center, and thus the failure of the catalyst to give isopropylidenecyclohexane is suggestive of an oxidative addition/ß–elimination pathway. In particular it may be noted that radical or carbonium ion mechanisms would be expected to yield isopropylidene cyclohexane as the major product. In this context we also note that in none of the alkane reactions is there any evidence of radical reactions such as dimer formation or H/D scrambling (discussed below).

Intermolecular selectivity

Irradiation of 1 in a 50:50 mixture of cyclooctane/cyclohexane under 400 torr CO yields cyclooctene and cyclohexene in a ratio of 130:1. This represents a kinetic product ratio, as demonstrated by the observation that irradiation (16 h) of a cyclooctane solution of 1 and cyclohexene (25 mM) afforded no detectable (< 0.2 mM) cyclohexane i.e. cyclohexene is not hydrogenated under the conditions of the reaction. Note that Bergman has found that the insertion of $(C_5Me_5)IrP$ into C–H bonds favors *cyclohexane over cyclooctane* by a factor of 11.[17]

Although under kinetic control, the alkylcyclohexane reactions show a preference for formation of the thermodynamically more stable olefins, with some mitigating effect of steric factors.[12] The cycloalkane competition experiment reveals a strong selectivity for the alkane which is thermodynamically more easily dehydrogenated; ΔH of cyclooctane dehydrogenation is 23 kcal/mol versus 28 kcal/mol for cyclohexane. In this case there would appear to be no mitigating steric effects. These results strongly suggest that the turnover-limiting (irreversible) step of the dehydrogenations involves a transition state with some carbon-carbon double bond character. Rather than C–H addition to a metal center, a subsequent ß-elimination step may be turnover-limiting. Alternatively, a reversible ß-elimination step (k_{-3}) would also tend to favor the formation of thermodynamically stable olefins as "kinetic" products.

$$\mathrm{M} + \mathrm{RH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M(R)(H)} \tag{6}$$

$$\mathrm{M(R)(H)} \underset{k_{-3}\,?}{\overset{k_3}{\rightleftharpoons}} \mathrm{M(olefin)H_2} \xrightarrow{k_4} \text{products} \tag{7}$$

In the context of these reaction steps, it is perhaps not surprising that we observe a different selectivity pattern in the present system in comparison with previously reported, related, alkane dehydrogenation (or transfer-dehydrogenation) systems. Other reported systems involve third-row metals, especially iridium.[3-5] Reductive elimination of alkyl hydrides from rhodium (k_{-2}) tends to be much more facile than from analogous iridium systems.[18] If the rate of ß-elimination (k_3) for iridium is comparable to or greater than for rhodium (and it is probably greater in view of the greater tendency of 16-electron iridium centers to become 18-electron), then we would expect the selectivity of iridium systems to be dominated by the selectivity of C–H addition much more so than for rhodium. Iridium systems would therefore display a greater tendency than rhodium to give the least hindered olefins, in accord with observation.

Irradiation of **1** in a 1:1 (v:v) mixture of C_6D_{12}/C_6H_{12} revealed an unusually high isotope effect for reaction 2, $k_H/k_D = 5.3$. Kinetic isotope effects for C-H oxidative additions in other systems[18-20] are found to be much lower than this. The large effect we observe is not easily reconciled with C-H addition as the turnover-limiting step. It is consistent with a pathway such as that of eqs. 6 and 7, involving a reversible C-H oxidative addition and a subsequent ß-elimination, which would yield an overall isotope effect $(K_{2H}/K_{2D})(k_{3H}/k_{3D})$. Jones[19a] has found an equilibrium isotope effect of 2.7 for the addition of a benzene C-H bond to $(C_5Me_5)RhP$. If $K_{2H/2D}$ is likewise approximately 2.7, then a plausible kinetic isotope effect, k_{3H}/k_{3D}, of approximately 2, would give the resulting overall value of 5.3. We also note that no H/D scrambling was observed, in either the cyclohexane or cyclohexene (C_6H_{10}/C_6D_{10}), when the resulting solution was analyzed by GC/MS.[22]

Identification of the photoactive species

Several hypothetical mechanisms for reaction 2 can be constructed based on precedented reactions of related species. Crabtree has proposed a mechanism for iridium photodehydrogenation, in which H_2 loss is the photochemical step, which is essentially the reverse of a typical thermal hydrogenation cycle.[5] Note that in the case of the present catalyst, **1**, a plausible cycle of such type must be photochemically *initiated*, i.e., one photon is necessary to enter the cycle and another photon is necessary to perpetuate it.

The mechanism shown in Figure 1 involves RhP_2H_2Cl as the photoactive intermediate. Known analogues of this complex are orange,[23] and therefore likely absorb light in the visible region more strongly than does the pale yellow **1**. Thus, it would be plausible that in experiments using a cutoff filter (e.g. Pyrex, $\lambda > 300$ nm) and a typical UV irradiation source (e.g. a Hg-arc lamp) the UV light irradiates the precursor 1 while the "catalytically active" intermediate can absorb the remaining visible light. To test this hypothesis, we irradiated a cyclooctane solution of 1 (under 800 torr CO) with two beams of light simultaneously. One beam was of UV light (366 nm) which is strongly absorbed by 1. The second beam was of visible light ($\lambda > 430$ nm) to which 1 is completely transparent. There was no significant acceleration from the visible light as compared with the UV light alone.[12]

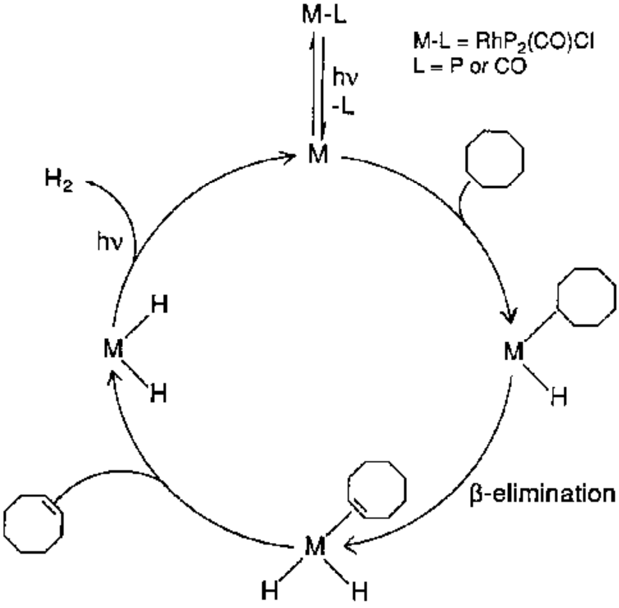


Fig. 1. Hypothetical mechanism for reaction 2 involving a photoactive intermediate.

In the case of monochromatic irradiation (366 nm) we can demonstrate that any cycle of the general form of that of Fig. 1 is not operative. Such a pathway requires an intermediate which absorbs 366 nm light strongly enough to be competitive with 1. Because the quantum yield of reaction 2 is fairly high, such an intermediate must absorb fairly strongly, for example 8% of the incident light under 50 torr CO at 50° ($\text{Ø}_{obs} = 0.08$). It would therefore be easily detectable by UV-visible spectroscopy. However, we have found that upon 366 nm irradiation of a cyclooctane solution of 1 (4.0×10^{-4} M) in a specially modified UV-visible spectrophotometer, no significant change ($< \pm 0.5\%$) of absorption at 366 nm (or 333 and 450 nm) is observed approximately 1.5 s after termination of irradiation.

It would still be plausible, *a priori*, that a strongly UV-absorbing species is a photoactive intermediate, but that it undergoes thermal decay too fast to be observed by our techniques. The most straightforward argument against this hypothesis relies on the fact that we can set an upper limit for the rate of formation of any intermediate, **X**: the rate at which photons enter the solution (eq 8). In order to escape detection by our methods, a species which absorbs 8% of the incident light during irradiation would require a half life (in the dark) of ≤0.4 s, i.e. $k_{-8} \geq 1.7\ s^{-1}$.

$$1 \underset{\Delta\ \ k_{-8}}{\overset{h\nu}{\rightleftharpoons}} X \qquad (8)$$

$$X \xrightarrow{h\nu} \text{products} \qquad (9)$$

The rate of eq 9 is simply the rate of product formation (8% of the photon flux where $\varnothing_{obs} = 0.08$). Using these parameters we can calculate the *maximum* steady state concentration of X (assuming a quantum yield of 1.0 for the formation of X) at the lowest experimental light intensity (I) of 1.3×10^{-9} Ein s^{-1} (in 1.6 mL, V) as $[X] = 4.4 \times 10^{-7}$ M.

$$\begin{aligned}[X] = [(\phi_8 - 0.08)(I/V)]/k_{-8} &= (\phi_8 - 0.08)(8.13 \times 10^{-7}\ M\ s^{-1})/k_{-8} \\ &\leq 0.92\ (8.13 \times 10^{-7}\ M\ s^{-1})/1.7\ s^{-1} = 4.4 \times 10^{-7}\ M \qquad (10)\end{aligned}$$

To absorb 8% of the incident light in competition with **1** (which is present at levels of $4.0 - 20 \times 10^{-4}$ M, $\varepsilon = 4500\ M^{-1}\ cm^{-1}$) would require an extinction coefficient of $3.3 \times 10^5\ M^{-1}\ cm^{-1}$,[24] whereas 10^5 $M^{-1}\ cm^{-1}$ may be taken as a reasonable maximum value.[25]

A different argument against the possibility of a thermally short-lived photoactive intermediate can be based on our observations that the quantum yield of reaction 2 is independent of light intensity ($1.3 \times 10^{-9} - 2.8 \times 10^{-8}$ Ein s^{-1}) and of the concentration of **1** (0.2 - 5.0 mM). This is as follows:

If the thermal decay of X (k_{-8}) is significant (relative to the forward photoprocess of eq 9), then $\varnothing_{obs}$ must decrease with increasing [**1**] due to competitive absorption by the major species **1**. Similarly, decreasing irradiation intensity would decrease $\varnothing_{obs}$ since the rate of reaction 9 would decrease relative to the thermal decay, contrary to our observations.

If, on the other hand, the thermal decay of **X** were much slower than the forward photoprocess (eq 9), we would be able to observe X in spite of the time delay between irradiation and observation. This is proven as follows. With a solution volume of 1.6 mL and an irradiation intensity of 1.30×10^{-9} Ein s^{-1}, for example, reaction 9 (product formation) proceeds at a rate of 6.5×10^{-8} mol $L^{-1}\ s^{-1}$. A thermal process much slower than reaction 9 would destroy much less than 9.8×10^{-8} mol L^{-1} of **X** in a delay time of 1.5 s; therefore the concentration of **X** during irradiation must be much less than this value in order to escape detection 1.5 s subsequently. For a species in such a concentration to absorb 8% of the incident light in competition with **1** (which is present at levels of $4.0 - 20 \times 10^{-4}$ M, $\varepsilon = 4500\ M^{-1}cm^{-1}$) would require an extinction coefficient, $\varepsilon_X >> 1.5 \times 10^6\ M^{-1}cm^{-1}$,[24] an implausibly high value.[25]

These observations conclusively demonstrate that complex **1** is the only important photoactive species in the dehydrogenation reaction of cyclooctane with 366 nm irradiation.[12] (Note that if we extrapolate from flash photolysis results with **1** and cyclohexane or benzene[10d] we would expect a slight bleaching effect upon irradiation, barely detectable with our system. This would imply the same conclusion, that there is no photoactive intermediate.)

Kinetics and mechanism of reaction 2

The quantum yield (λ = 366 nm) or rate[26] (λ > 300 nm) of reaction 2 (50° C, [**1**] = 2.0 mM) is found to be independent of H_2 partial pressure[27] and cyclooctene concentration over the ranges 0-2400 torr H_2 (400 torr CO), and 0 - 0.4 M cyclooctene (400 torr H_2, 400 torr CO). Although the enthalpies of the alkane dehydrogenation reactions are highly positive it has been claimed[28] that they proceed through a photochemically initiated thermochemical cycle. However our observation that reaction 2 proceeds under hydrogen (which would give under one atmosphere at equilibrium,[15] [cyclooctene] = 6×10^{-10} M) is completely inconsistent with this proposal.

The quantum yield (λ = 366 nm, 50° C, P_{H_2} = 400 torr) of the cyclooctane dehydrogenation shows a Stern-Volmer dependence on the partial pressure of carbon monoxide (i.e. a plot of $1/Ø_{obs}$ vs. P_{CO} is linear) over the range P_{CO} = 0-2700 torr (Figure 2).[29]

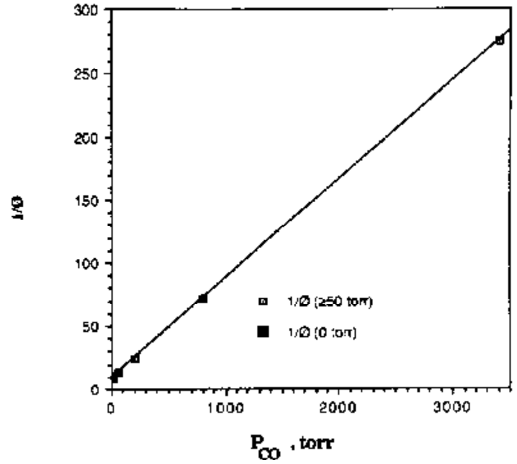


Fig. 2. Dependence of the quantum yield of reaction 2 (λ = 366 nm, 50 °C) on P_{CO}; $[RhP_2(CO)Cl]$ = 2.0 mM; P_{H_2} = 400 Torr; neat cyclooctane

Although an excess of trimethylphosphine reacts with **1**, we found that addition of less than ca. one equivalent of PMe_3 has no significant effect on either the infrared or UV-visible spectra of a solution of **1**. The presence of up to one equivalent (2 mM) trimethylphosphine was found to have no effect on the quantum yield of reaction 2. (More than about one equivalent resulted in the formation of a precipitate, presumably either P_3RhCl or $[P_4Rh]Cl$.)

The above photokinetic and selectivity data are consistent with a mechanism involving reversible CO loss from **1**, followed by reversible addition of a C-H bond, and subsequent ß-hydrogen elimination to give $RhP_2Cl(alkene)H_2$. The alkene dihydride complex could then lose alkene to give an unsaturated dihydride which could react with carbon monoxide (added or photoliberated) to displace dihydrogen and regenerate **1**. Alternatively, an analogous pathway involves loss of dihydrogen from the alkene dihydride complex, followed by reaction with carbon monoxide to displace alkene. These alternative pathways (designated **a** and **b**) are shown in Figure 3.

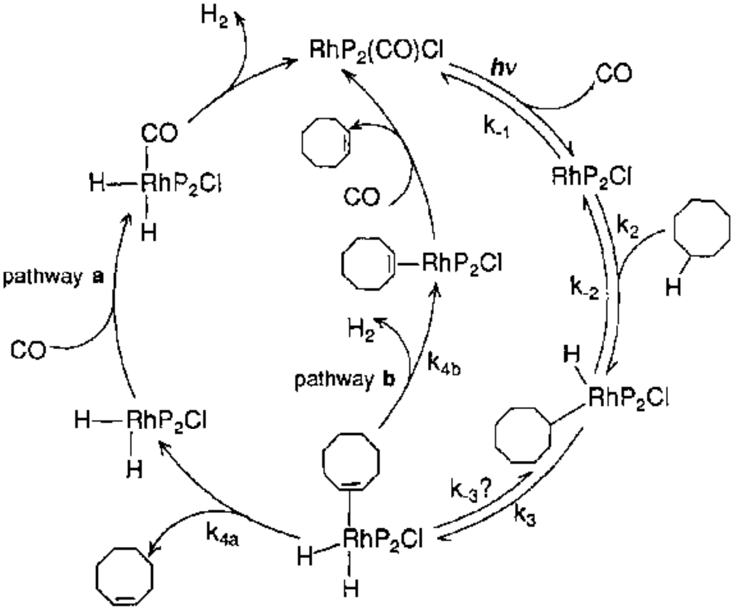


Fig. 3. Two variations (**a** and **b**) of the proposed mechanism of reaction 2.

The quantum yield predicted on the basis of this mechanism (either pathway **a** or **b**) is expressed in equation 11 (where ø is the primary quantum yield for the formation of free RhP_2Cl).

$$\O_{obs} = \frac{\o\, k_2[C_8H_{16}]k_3k_4}{k_{-1}[CO](k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4) \; + \; k_2k_3k_4[C_8H_{16}]} \qquad (11)$$

To determine the dependence of the reaction rate on cyclooctane concentration a series of experiments was performed in which **1** was irradiated in solvent mixtures of varying cyclooctane/cyclohexane ratios. The rate of cyclooctene formation was found to depend on [cyclooctane], although with some deviation (< 20%) from from eq 11. The observed deviation is not surprising since cyclohexane is not genuinely chemically inert.

The various rate constants in eq 11 are expected to be strongly dependent on the particular alkane substrate. However, in the absence of CO, eq 11 reduces to $Ø_{obs} = ø$, the primary quantum yield for CO loss, which should not vary significantly with different alkanes. We therefore briefly examined the quantitative behavior of cyclohexane, a substrate found to be much less reactive than cyclooctane in competition experiments as described above. In the absence of added CO the quantum yield for cyclohexane dehydrogenation (argon atmosphere) is identical to that found for cyclooctane ($Ø_{obs} = 0.097$).[29,30] A plot of 1/rate vs. P_{CO} (0 - 2400 torr) for cyclohexane[30] dehydrogenation is found to be linear with a slope much greater than that found for cyclooctane, as expected. These results are strongly supportive of our interpretation of Fig. 2, in particular that the limiting value of $Ø_{obs}$ is equal to ø, the quantum yield of the primary photoprocess (photoextrusion of CO).

TRANSFER-DEHYDROGENATION

We wished to determine which of the two pathways of Fig. 3 was operative, and in addition, to investigate the later steps of the catalytic cycle (subsequent to the turnover-limiting step). In particular we sought direct evidence for substitution by CO of either olefin or H_2, since we view this step (in conjunction with Rh-CO photolysis) as the one which drives the reaction "uphill". We turned our attention toward a reaction which we had observed in previous studies, transfer-dehydrogenation.[22]

$$\text{n alkane} + \text{m } H_2C{=}CHR \xrightarrow{1 \quad h\nu} \text{n alkene} + \text{m } H_3C\text{-}CH_2R + (\text{n-m}) H_2 \qquad (12)$$

Mass spectrometry (GC/MS) revealed that even under D_2 atmosphere, the reaction of cyclooctane, where R = Bu^t, proceeded to give entirely hydrogenated product (t-butylethane). No significant incorporation of deuterium was observed in either the products or unreacted starting materials.[22] For example, less than 2% t-butylethane-d_2 was observed to form under an atmosphere of 1500 torr D_2 and 200 torr CO. Thus, the transfer of two hydrogen atoms from cyclooctane to t–butylethylene does *not* proceed *via* the formation of free H_2 and subsequent hydrogenation of olefin. If we assume that the transfer of hydrogen from rhodium to the olefin acceptor must proceed via an *unsaturated* dihydride,[31] then pathway **b** as it appears in Fig. 3 is not consistent with the observed lack of deuterium incorporation in the t–butylethane. However pathway **a** is entirely consistent with this result, which suggests that RhP_2ClH_2 can react with t–butylethylene to give t–butylethane.

In the *absence* of added carbon monoxide the transfer-hydrogenation proceeds with high efficiency, i.e., nearly one mole of t-butylethane is formed for every mole of cycloctene, and little dihydrogen is evolved (n – m in eq 12; the exact results are as yet somewhat irreproducible). In the presence of added carbon monoxide, H_2 is produced in quantities much greater than t-butylethane (as quantified below).[22] These observations are suggestive of a competition between carbon monoxide and t-butylethylene for an H_2-containing species. This is consistent with dehydrogenation pathway **a**, as indicated in Fig. 4.

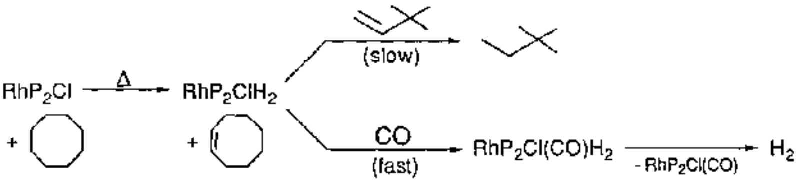


Fig. 4. In the absence of CO, t-butylethylene is efficiently hydrogenated, probably via the upper pathway; in the presence of added CO the lower pathway predominates, suppressing transfer-hydrogenation. Lower pathway constitutes part of pathway a, Fig. 3.

The ratio of H_2 to hydrogenated product (e.g. t-butylethane) formed in eq 12, is defined as $Q = (n - m)/m$. Monitoring the value of Q enabled us to quantitatively probe the later steps of the mechanisms of transfer-dehydrogenation and photodehydrogenation. In particular we could investigate the nature of the "branching intermediate", which we define as the last intermediate common to both pathways, and the "branching steps", defined as the reactions of the branching intermediate leading to hydrogenated olefin and H_2 respectively. For these studies we generally used styrene instead of t- butylethylene, in order to avoid complications due to the high volatility of t -butylethylene and t-butylethane at 50 °C.

As would be expected based on the schemes of Fig. 3 and Fig. 4, Q is independent of the concentration of cyclooctane concentration (25 -100%) in cyclohexane solvent (5% styrene; $P_{CO} = 50$ torr). Q (5% styrene, $P_{CO} = 50$ torr) is also found to be independent of light intensity over a ten-fold range achieved with a neutral density (OD =1.0) filter,[26] and in preliminary experiments, independent of irradiation wavelenth (broad-band $\lambda > 340$ nm versus $\lambda = 366$ nm).[22] The latter observations indicate that both pathways share a common photochemical step, i.e., Rh-CO bond photolysis. In particular the intensity-independence is inconsistent with a competition between photochemical versus thermal reactions of an intermediate such as RhP_2ClH_2, leading to the formation of H_2 and ethylbenzene (hydrogenated styrene) respectively.

The value of Q is also found to be independent of the nature of the hydrogen donor. A 5% styrene solution under 50 torr CO gave values of Q identical within experimental error with the following hydrogen-donor systems: cyclooctane (3.17), cyclohexane (3.53), and 5% isopropanol/cyclohexane-d_{12} (3.59; acetone was the only observed dehydrogenated product). This result very strongly implies that the branching intermediate does not contain the dehydrogenated product molecule (cyclooctene, cyclohexene, or acetone). This is further evidence against pathway **b** which involves no metal hydrides that do not contain dehydrogenated product. The results are consistent with the identity of the branching intermediate as one of the species of pathway **a** subsequent to alkene dissociation, i.e., RhP_2ClH_2 or $RhP_2Cl(CO)H_2$.

Although Q increases dramatically upon addition of 50 torr CO pressure, Q is independent of CO pressure *above* 50 torr. Similarly, under 50 or 400 torr CO pressure, Q is nearly independent of styrene concentration above ca. 5% styrene. Preliminary results indicate that in the realm of saturation in hydrogen acceptor concentration, the value of Q is also independent of the *nature* of the acceptor (cycloheptene, styrene, t-butylethylene, 1-pentyne).[22] These results are inconsistent with Fig. 4 as a description of the branching steps *under CO atmosphere* (above 50 torr). Instead, the observed saturation in CO pressure suggests that even in the presence of olefin, RhP_2ClH_2 reacts rapidly with CO (≥50 torr) to give $RhP_2ClH_2(CO)$. In analogy with other six-coordinate rhodium(III)dihydrido-phosphine species, loss of either H_2 or phosphine can follow (Fig. 5). For example phosphine dissociates from $Rh(PPh_3)_3ClH_2$, (in this case much faster than H_2 eliminates) and leads to olefin hydrogenation.[31] We propose that the observed branching step in the realm of "high" CO and high olefin concentration is the analogous intramolecular competition, as shown in Fig. 5.

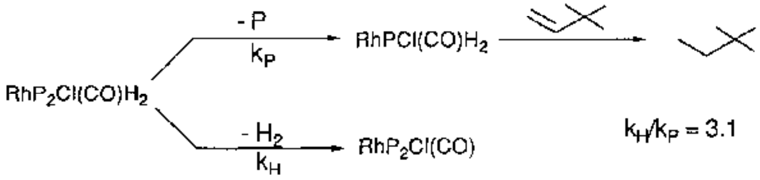


Fig. 5. Proposed "branching step" under CO atmosphere.

The observed temperature-dependence of Q is consistent with the idea that the value of Q in the realm of high P_{CO} and high [olefin] is determined by the competion of Figure 5. *A priori*, it might be expected that the rate-limiting step for hydrogenation would involve an ordered configuration which would include coordinated or incoming olefin, while that for dehydrogenation would involve H_2 dissociation. However, a plot of ln Q versus 1/T yields a straight line, of which the intercept should represent $\Delta\Delta S^{\neq}$, the difference in activation entropies of the two branches. The relatively low value found, $\Delta\Delta S^{\neq} = 10$ e.u.,[22] appears to be inconsistent with a competition between H_2 loss and an olefin-hydrogenation step. Instead, this low value appears to be consistent with a competition between two, intramolecular, dissociative reactions as indicated in Fig. 5.

Related chemistry of $[RhP_2Cl]_2$

In view of the importance of RhP_2Cl as a proposed intermediate in reactions 2 and 3, we have begun to examine the chemistry of the isolable dimer of this species, $[RhP_2Cl]_2$. This dimer reacts immediately with carbon monoxide to yield two moles of **1**. When a mole of dimer is exposed to two moles of H_2, ^1H NMR spectrometry reveals a complex mixture containing at least 6 different phosphine- and hydrogen-containing species which have so far eluded characterization. (An excess of H_2 results in a somewhat different, but equally complex, mixture.) Very likely, some of these species are of the form $[RhP_2ClH_2]_n$. When the hydride mixture is exposed to CO, it is immediately and completely converted to **1** (Fig. 6). The hydride mixture was also found to hydrogenate various olefins (in the absence of CO) (Fig. 6).

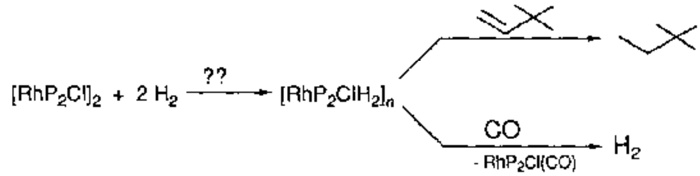


Fig. 6. Reactivity of hydride mixtures obtained from addition of H_2 to $[RhP_2Cl]_2$.

These results led us to consider the possibility that RhP_2ClH_2, formed from alkane dehydrogenation, could dimerize or oligomerize in the course of reactions 2 and 3. The observed photo- and transfer-dehydrogenation behavior in the absence of added CO is not inconsistent with this possibility. It is plausible that the RhP_2ClH_2 dimers/oligomers could hydrogenate t-butylethylene if present, or ultimately react with photoliberated CO in the absence of hydrogen-acceptor. If this is the case, the scheme of Fig. 4 is essentially valid except that the reactions shown therein do not actually involve the monomer itself, RhP_2ClH_2, directly.

The chemistry of $[RhP_2Cl]_2$, however, does not seem consistent with dehydrogenation pathways involving RhP_2ClH_2 dimer/oligomers, in the *presence* of added CO. The independence of Q on P_{CO} and on the nature and concentration of olefin would seem difficult to reconcile with such pathways. In addition, the rate of RhP_2ClH_2 formation (i.e. the rate of dehydrogenation) in our experiments varies greatly depending on factors such as light intensity and P_{CO}. Any competition between dimerization/oligomerization of RhP_2ClH_2 versus reactions with either CO or with olefin should be affected by the rate of RhP_2ClH_2 formation, and would in turn affect the value of Q, in contrast with our observations. Furthermore, varying the rate of RhP_2ClH_2 formation could also affect the nature of dimerization/oligomerization products, which would be expected to influence the value of Q. Thus on the basis of our present data, in the presence of added CO there seems to be no role of di- or polynuclear intermediates in reactions 2 and 3.

CONCLUSION

Alkanes are photocatalytically converted to alkenes by $RhP_2Cl(CO)$. H_2 is evolved or, in the presence of potential hydrogen acceptors such as t-butylethylene and styrene, hydrogen can be transferred to the olefins. Labeling studies demonstrate that the transfer-hydrogenation does not proceed via free H_2.

The mechanism of these two reactions, alkane dehydrogenation (yielding free H_2) and transfer-dehydrogenation, has been studied. Loss of CO from $RhP_2Cl(CO)$ is the only photoprocess involved. RhP_2Cl, the resulting 14-electron species, undergoes reversible C-H bond oxidative addition, followed by ß-hydrogen elimination, to give a species of the form RhP_2ClH_2(alkene). We have studied the relative extent of H_2 evolution and olefin hydrogenation as a function of several parameters, including the nature and concentration of hydrogen-donor, the nature and concentration of hydrogen-acceptor, CO pressure, irradiation intensity and wavelength, and temperature. The results of these experiments have enabled us to determine that hydrogenation of the olefinic hydrogen-acceptors occurs subsequent to loss of alkene from RhP_2ClH_2(alkene). This conclusion is consistent with only one of two previously viable pathways for photodehydrogenation.

The pathway leading to olefin (transfer-)hydrogenation is fairly complicated (as is the known behavior of related hydrogenation catalysts[31]). The mechanism has not yet been fully elucidated, but under CO atmosphere it appears that loss of phosphine from $RhP_2Cl(CO)H_2$ is the rate-limiting step.

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24 The fraction of incident light absorbed by **X** in a solution of **1** and **X**, is equal to $(1-T_{total})\varepsilon_x c_x/(\varepsilon_x c_x + \varepsilon_1 c_1)$. Since T< 0.016 in all cases (due to absorption by 1), this term is approximately equal to $\varepsilon_x c_x/(\varepsilon_x c_x + \varepsilon_1 c_1)$. We know that $c_1 \geq 4 \times 10^{-4}$ M, and $\varepsilon_1 = 4500\ M^{-1}cm$. If the thermal reaction is much slower than the forward photoreaction ($6.5 \times 10^{-8}\ M\ s^{-1}$), the concentration disappearance of **X** is << 9.8×10^{-8}M in 1.5 s. This quantity must absorb ≥8% of the incident light minus the limit of our detection, 0.5%. Thus

$\varepsilon_x c_x/(\varepsilon_x c_x + \varepsilon_1 c_1) \geq 0.075$ which can be rearranged to $\varepsilon_x c_x \geq 0.081\ (\varepsilon_1 c_1)$.

$\varepsilon_x >> (0.081)\ \varepsilon_1 c_1/(9.8 \times 10^{-8}M) = 1.5 \times 10^6\ M^{-1}\ cm^{-1}$.

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29 The reciprocal quantum yield for reaction 2 with cyclooctane in the absence of CO (Ø = 0.097; 1/Ø = 10.3) deviates slightly from the calculated intercept, 9.4. This deviation, which is more pronounced in broadband irradiation experiments, may be attributed to the formation of $Rh_2P_4Cl_2$ due to loss of CO under these conditions.

30 Because the cyclohexane dehydrogenations *under CO atmosphere* were very slow, broadband irradiation was used and quantum yields were not measured. Additionally, a 500W Hg–arc lamp was used instead of the 200W Hg/Xe–arc lamp used for the cycloctane dehydrogenation and therefore the 1/rate vs. P_{CO} slopes for the two substrates may not be quantitatively comparable.

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