

Kinetics of photochemical alkane dehydrogenation catalyzed by $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$: implications concerning the C–H bond activation step

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Abstract

The mechanism of photochemical alkane dehydrogenation catalyzed by $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ has been further probed with an emphasis on characterizing the initial C–H activation step and understanding the effect of added CO on selectivity. While pure cyclooctane and pure cyclohexane are dehydrogenated at the same rate (same quantum yields), cyclooctane shows much greater reactivity in mixtures of the two solvents. The product ratio (cyclooctene:cyclohexene) is highly dependent upon the partial pressure of CO, ranging from 12 in the absence of CO, to 75 in the limit of high CO pressure (> ca. 400 torr). The kinetic isotope effect for the dehydrogenation of $\text{c-C}_6\text{H}_{12}/\text{c-C}_6\text{D}_{12}$ is also found to be dependent upon CO pressure, ranging from 10 in the absence of CO to 4.2 under high CO pressure. The results support our earlier conclusion that the intermediate responsible for C–H activation is ground state $[\text{Rh}(\text{PMe}_3)_2\text{Cl}]$. It is also concluded that inhibition of the reaction by CO operates primarily via addition of CO to the intermediate alkyl hydrides, $(\text{R})(\text{H})\text{Rh}(\text{PMe}_3)_2\text{Cl}$. Addition of CO prior to C–H bond addition is apparently not a kinetically significant process, even under high CO pressure. © 1998 Elsevier Science S.A.

Keywords: Dehydrogenation; C–H bond activation step; CO pressure

1. Introduction

The photochemical dehydrogenation of alkanes catalyzed by $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ (Eq. (1)) could be considered the first reported example of efficient (> ca. 100 catalytic turnovers) alkane functionalization catalyzed by a soluble low-valent transition metal complex (for the first example of alkane photodehydrogenation catalyzed by soluble metal complexes, [1–4].



Since alkane dehydrogenation is a highly endothermic process (ca. 23–32 kcal/mol) [5], the role of light in this reaction is necessarily more than to merely generate a reactive thermochemical catalyst (via metal–ligand bond cleavage, for example). Instead of simply providing entry into a catalytic cycle, one or more photochemical steps must be contained *within* the cycle.

Several years ago we proposed the catalytic cycle shown in Fig. 1 [4].

Key features of the mechanism of Fig. 1 include the following points: (i) cleavage of the Rh–CO bond is the only photochemical step in the cycle; (ii) ground state RhL_2Cl ($\text{L} = \text{PMe}_3$) undergoes addition to the alkane; (iii) addition to the alkane is reversible.

Reaction 1 is inhibited by added CO atmosphere [4]. Clearly, the most straightforward explanation for this observation, in terms of Fig. 1, involves addition of CO to RhL_2Cl , i.e. the reverse of the photochemical step. The possibility that CO *also* inhibits dehydrogenation via addition to the presumed rhodium alkyl hydride intermediate was also considered. However, if CO adds to two kinetically distinct intermediates in the cycle, the inhibition would be expected to show an inverse second-order term in [CO]. Since the inhibition very clearly showed only an inverse-first order term (Stern–Volmer kinetics), it was assumed that CO addition to the alkyl hydride is not a kinetically significant process [4].

Herein we report on photokinetic studies designed to provide a more in-depth understanding of the initial

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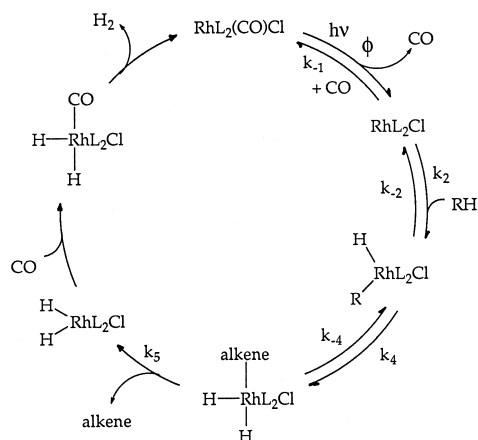


Fig. 1. Previously proposed mechanism for reaction 1.

steps in the catalytic cycle of reaction 1. The results provide further support for the points (i)–(iii) discussed above. However, this work indicates that the assumed mode of inhibition by CO, simple back reaction with RhL_2Cl , is *not* a kinetically significant process. Instead, addition to the rhodium alkyl hydride accounts for the inhibition by CO. Assuming that the reaction of free RhL_2Cl with CO would be quite facile, this implies that addition of C–H bonds to RhL_2Cl is both kinetically very facile and thermodynamically very favorable.

2. Results and discussion

2.1. Photochemical dehydrogenation of cyclooctane / cyclohexane

In the absence of CO atmosphere, irradiation of solutions of **1** (2.0 mM, $\lambda > 280$ nm, 50°C) in either cyclooctane (COA) or cyclohexane (CHA) gives identical reaction rates for formation of the corresponding alkene (0.27 mM/min).¹ With monochromatic irradiation,

¹ These rates were obtained with the use of a neutral density filter (OD = 1.0; 10% transmittance). Without such a filter the rates for cyclooctane dehydrogenation are approximately 10-fold faster, as would be expected; however, the rate of cyclohexane dehydrogenation in the absence of CO atmosphere is only about a factor of 2 faster (and reproducibility is poor). Under 50 torr CO both solvents show the expected 10-fold difference. The unusual intensity-dependence for cyclohexane may be attributed to residual CO being present during high-intensity (unfiltered) irradiation: either due to a higher steady-state concentration of CO or perhaps CO liberated by product decomposition. Cyclohexane is expected to show a much greater sensitivity to residual CO, considering that 50 torr CO (ca. 0.5 mM) lowers the cyclohexane dehydrogenation rate by a factor of 60 while the cyclooctane rate is lowered only by a factor of 2. Alternatively, the intensity-dependence for cyclohexane may be attributed to reactions other than CO addition competing with dehydrogenation. For example, dimerization of $\text{RhL}_2\text{Cl}(\text{R})(\text{H})$ (followed by loss of RH), if it occurs, would be most significant when the alkyl hydride only slowly undergoes β -hydrogen elimination and under conditions of very low CO pressure and high irradiation intensity.

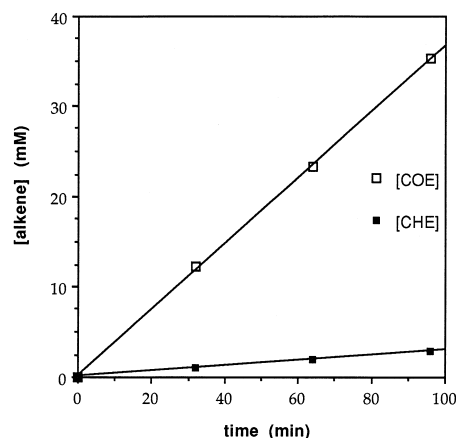


Fig. 2. Dehydrogenation of 1:1 COA/CHA under argon atmosphere.

tion, 366 nm, the quantum yields were determined to be 0.097(4) [4]. However, when a 1:1 COA/CHA solvent mixture was used, cyclooctene (COE) was formed 12.5-times as rapidly as cyclohexene (CHE; see Fig. 2) [4]. The mechanism of Fig. 1, as it would operate in a two-solvent system, is shown in Fig. 3.

In addition to such competition experiments, greater reactivity of cyclooctane is also observed with pure solvents under CO atmosphere. For cyclooctane, a plot of $1/\Phi$ vs P_{CO} gives a straight line (Stern–Volmer dependence) over the range 0–3400 torr with an intercept of 9.4 and a slope of 0.080 torr^{-1} [4]. For cyclohexane the rate of reaction under CO is too slow to obtain good measurements using monochromatic light; using broad-band irradiation ($\lambda > 280$ nm), however, a

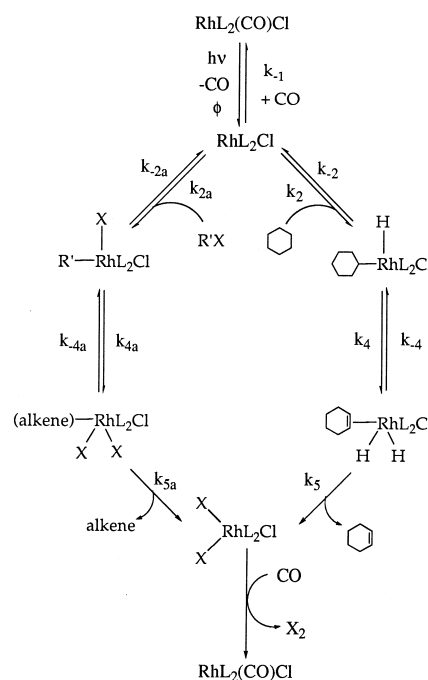


Fig. 3. The dehydrogenation mechanism of Fig. 1, adapted to a two-solvent system ($\text{R}' = \text{cyclooctyl}$, $\text{X} = \text{H}$; or $\text{R}' = \text{C}_6\text{D}_{11}$, $\text{X} = \text{D}$).

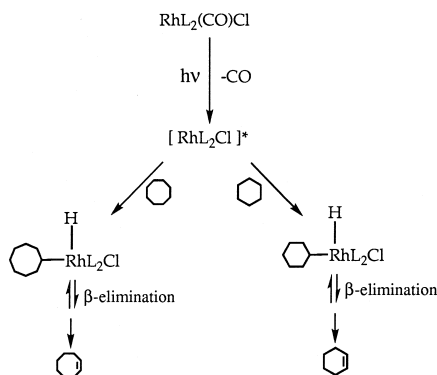


Fig. 4. Hypothetical (invalid) excited state mechanism for alkane photodehydrogenation.

plot of $1/\text{rate}$ vs. P_{CO} is also found to be linear. For direct comparison, the rates of dehydrogenation of CHA and COA were measured under 50 torr CO and under identical conditions; they were found to be 0.13 mM/min and 0.0042 mM/min respectively (cf. 0.27 mM/min for both solvents in the absence of CO atmosphere; see footnote).

The fact that pure cyclooctane and cyclohexane are dehydrogenated with equal quantum yields in the *absence* of CO is consistent with a rate-determining step under such conditions which does not involve the alkane, i.e., photoextrusion of CO from **1**. Thus both cyclooctane and cyclohexane undergo dehydrogenation with unit efficiency after photolysis of **1** in the absence of CO [4]. In mixed-solvent systems a competition between alkanes take place. With pure solvents under CO atmosphere, there is a competition between a reaction with CO and the reaction with alkane. The greater reactivity of COA vs. CHA is probably related to the lower dehydrogenation enthalpy of COA (23.3 kcal/mol versus 28.2 kcal/mol for cyclohexane [5]) and/or, perhaps, the more crowded geometry of the eight-membered ring which could facilitate access of the metal center to a β -hydrogen atom. In either case, we may

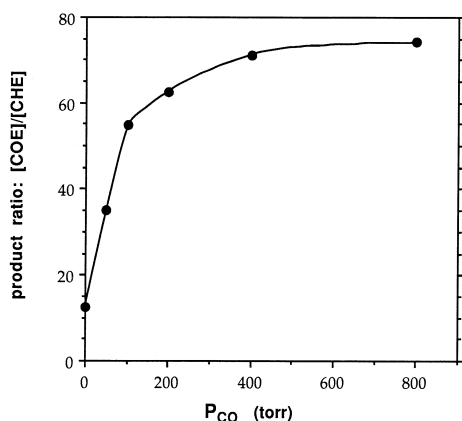


Fig. 5. Ratio of COE/CHE formation as a function of CO pressure.

assume that β -H elimination is more favorable for the cyclooctyl hydride (kinetically and/or thermodynamically).

The greater reactivity of cyclooctane *cannot* reasonably be attributed to a greater tendency to undergo C–H bond addition; indeed Bergman has found that the insertion of $(\text{C}_5\text{Me}_5)\text{IrL}$ into C–H bonds favors *cyclohexane over cyclooctane* by a factor of 11 [6]. Furthermore, a greater tendency to undergo C–H bond addition could not explain the selectivity enhancement effected by CO (vide infra).

The selectivity for cyclooctane observed in mixed-solvent competition experiments requires that the photo-generated species must be capable of an initial reaction with cyclohexane, followed by cyclohexane loss and reaction with cyclooctane to give cyclooctene. Significantly, this rules out a mechanism in which the species that activates the alkane must be a photoexcited state as in Fig. 4.

The observations noted above can all be explained in terms of the mechanism of Fig. 1 and Fig. 3. In contrast, however, the results of competition experiments under *varying* CO pressures are not easily reconciled with this mechanism. Increasing CO pressure results in increasing the COE/CHE ratio, from 12.5:1 in the absence of CO, to ca. 75:1 in the limit of high CO pressure (Fig. 5). According to the mechanism of Fig. 3, however, the COE:CHE product ratio is predicted to be independent of $[\text{CO}]$ (Eq. (2)).

$$\frac{d[\text{COE}]/dt}{d[\text{CHE}]/dt} = \frac{[\text{COA}]k_{2a}k_{4a}k_{5a}(k_{-2}(k_{-4} + k_5) + k_4k_5)}{[\text{CHA}]k_2k_4k_5(k_{-2a}(k_{-4a} + k_{5a}) + k_{4a}k_{5a})} \quad (2)$$

The observed dependence of the COE:CHE ratio on P_{CO} can, however, be reconciled with a mechanism in which the respective alkane adducts react with CO in competition with dehydrogenation. Such a mechanism is shown in Fig. 6.

If one assumes steady state conditions for all of the intermediates, the mechanism of Fig. 6 yields the following equation for the COE:CHE product ratio.

$$\frac{d[\text{COE}]/dt}{d[\text{CHE}]/dt} = \frac{[\text{COA}]k_{2a}k_{4a}k_{5a}(k_{-2}(k_{-4} + k_5) + k_4k_5 + k_3(k_{-4} + k_5)[\text{CO}])}{[\text{CHA}]k_2k_4k_5(k_{-2a}(k_{-4a} + k_{5a}) + k_{4a}k_{5a} + k_{3a}(k_{-4a} + k_{5a})[\text{CO}])} \quad (3)$$

In the limits of low and high CO pressure, Eq. (3) reduces to Eq. (4) and Eq. (5), respectively,

$$\frac{d[\text{COE}]/dt}{d[\text{CHE}]/dt} = \frac{[\text{COA}] k_{2a} k_{4a} k_{5a} (k_{-2} (k_{-4} + k_5) + k_4 k_5)}{[\text{CHA}] k_2 k_4 k_5 (k_{-2a} (k_{-4a} + k_{5a}) + k_{4a} k_{5a})} \times (\text{low CO pressure}) \quad (4)$$

$$\frac{d[\text{COE}]/dt}{d[\text{CHE}]/dt} = \frac{[\text{COA}] k_{2a} k_{4a} k_{5a} (k_{-4} + k_5)}{[\text{CHA}] k_2 k_4 k_5 k_{3a} (k_{-4a} + k_{5a})} \times (\text{high CO pressure}) \quad (5)$$

Thus, according to the mechanism of Fig. 6 the COE:CHE ratio is predicted to vary with increasing CO pressure, asymptotically approaching a value different from that observed in the low-[CO] limit, in accord with experimental results (Fig. 5).

It should be noted that the observed dependence of selectivity on [CO], particularly the saturation in [CO] which can be attributed to Eq. (3) reducing to Eq. (5), requires that Eq. (6) is obeyed in the CO-saturation regime ($> \text{ca. } 400 \text{ torr CO}$). This implies that CO addition is the major reaction undergone by the alkyl hydride in this regime.

$$k_3[\text{CO}] \gg k_{-2} + k_4 k_5 / (k_{-4} + k_5) \quad (6)$$

As noted in the introduction, it was previously reported that a plot of $1/\Phi$ vs. P_{CO} for COA dehydro-

genation is linear [4]. If we consider a scheme in which CO reacts with both RhL_2Cl (k_{-1}) and $\text{RhL}_2\text{Cl(R)(H)}$ ($k_3[\text{CO}]$) to inhibit product formation, the steady state kinetics yields the following expression (ϕ is the primary quantum yield for CO loss):

$$1/\Phi_{\text{obs}} = 1/\phi + K'k_{-1}[\text{CO}] [k_{-2} + k_4 k_5 / (k_{-4} + k_5)] + K'k_2 k_3[\text{CO}] + K'k_{-1} k_3[\text{CO}]^2 \quad (7)$$

where $K' = \phi k_2 k_4 k_5 [\text{COA}]$. According to Eq. (7), a plot of $1/\Phi_{\text{obs}}$ vs. [CO] will be non-linear unless one or both of the first-order terms is much greater than the second-order [CO] term. In fact, the second-order term is actually much greater than the first of the first-order terms since Eq. (8) can be reduced to Eq. (6).

$$K'k_{-1} k_3[\text{CO}]^2 \gg K'k_{-1}[\text{CO}] \times [k_{-2} + k_4 k_5 / (k_{-4} + k_5)] \quad (8)$$

Therefore, the dominant term in Eq. (7) must be $K'k_2 k_3[\text{CO}]$; in other words, those terms in Eq. (7) which represent the back reaction of RhL_2Cl with CO (i.e. those terms containing k_{-1}) are kinetically insignificant. More specifically, Eq. (10) follows from Eq. (9).

$$K'k_2 k_3[\text{CO}] \gg K'k_{-1} k_3[\text{CO}]^2 \quad (9)$$

$$k_2 \gg k_{-1}[\text{CO}] \quad (10)$$

Eq. (10) implies that the major reaction of RhL_2Cl is formation of alkyl hydride rather than back reaction with CO, even in the high pressure regime (ca. 400–3400 torr). In the same regime, the major reaction of the alkyl hydride is addition to CO (Eq. (6)). Thus, reaction of alkyl hydride with CO is kinetically much more important than the reaction of RhL_2Cl with CO.

2.2. Photochemical dehydrogenation of cyclohexane- d_{12} / cyclohexane

In an attempt to gain more information about the alkane activation step, reactions were conducted using a mixture of perprotio and perdeutero cyclohexane (50:50). In the absence of CO, a very high isotope effect is observed, $k_{\text{H}}/k_{\text{D}} = 10$. This provides further evidence against selectivity being determined by the relative rates of oxidative addition, and further argues against the mechanism of Fig. 4, since C–H(D) addition isotope effects are generally small (certainly much less than 10 in all known cases).

The effect of added carbon monoxide on the isotope effect was examined. As in the analogous COA/CHA competition experiments, the product ratio (in this case $\text{CHE-h}_{10}:\text{CHE-d}_{10}$) was found to be dependent upon

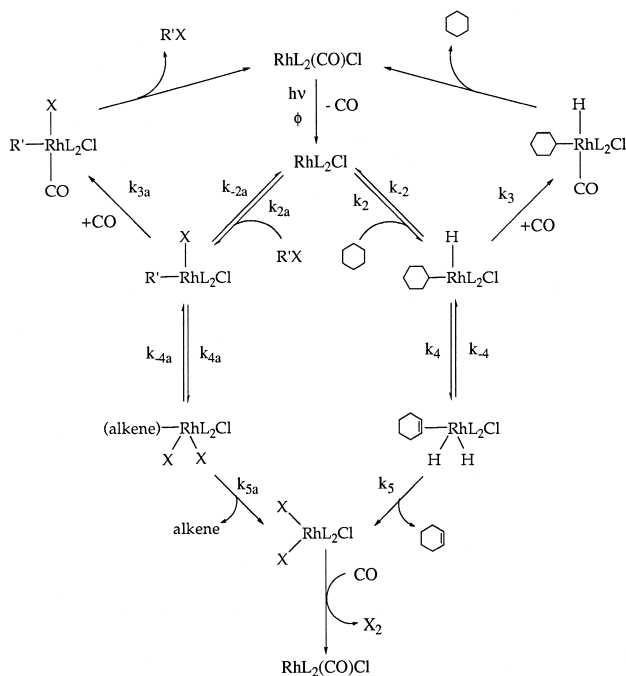


Fig. 6. Proposed photodehydrogenation mechanism (two-solvent system; R' = cyclooctyl, X = H; or R' = C_6D_{11} , X = D).

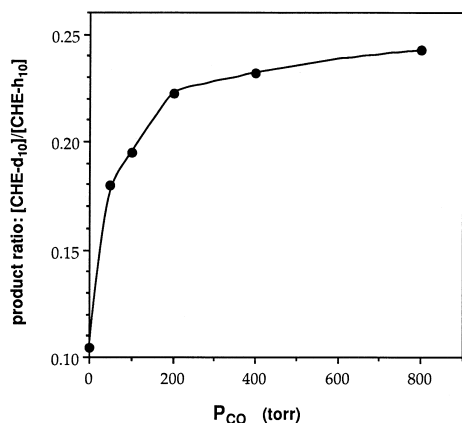


Fig. 7. Ratio of the rates of dehydrogenation of C_6D_{12}/C_6H_{12} vs. CO pressure.

CO pressure, decreasing from 10 to 4.2, with saturation observed at ca. 400 torr CO (Fig. 7). These results can also be interpreted in terms of Fig. 6. In this case since the alkane adducts should react with CO at essentially equal rates, we can assume that $k_3 = k_{3a}$ which simplifies the kinetic analysis.

To account for the COA:CHA competition results, as well as the high isotope effect observed in competition experiments in the absence of CO, we must assume that reductive elimination from the alkyl hydrides is much faster than the subsequent rate-limiting step (i.e. there is a pre-equilibrium between the respective alkyl hydride isotopomers):

$$k_{-2} \gg k_4 k_5 / (k_{-4} + k_5) \text{ or } k_{-2}(k_{-4} + k_5) \gg k_4 k_5 \quad (11)$$

In the limits of low and high CO pressures, Eq. (3) (substituting CHE-d₁₀ for COE) reduces to Eq. (12) and Eq. (13), respectively

$$\begin{aligned} \frac{d[COE-d_{10}]/dt}{d[CH E-h_{10}]/dt} &= \frac{[C_6D_{12}] k_{2a} k_{4a} k_{-2} k_{5a} (k_{-4} + k_5)}{[C_6H_{12}] k_2 k_4 k_{-2a} k_5 (k_{-4a} + k_{5a})} \\ &= 0.10 \text{ (no CO)} \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{d[COE-d_{10}]/dt}{d[CH E-h_{10}]/dt} &= \frac{[C_6D_{12}] k_{2a} k_{4a} k_{5a} (k_{-4} + k_5)}{[C_6H_{12}] k_2 k_4 k_5 (k_{-4a} + k_{5a})} \\ &= 0.24 \text{ (high CO pressure)} \end{aligned} \quad (13)$$

Dividing Eq. (12) by Eq. (13) gives the kinetic isotope effect (KIE) for reductive elimination.

$$k_{-2}/k_{-2a} = 0.42$$

Thus a rather strongly inverse KIE is derived for alkane loss from the species which undergoes the kinetically significant reaction with CO. Inverse KIEs are not common, but certainly not unprecedented. In general they are observed when an H/D atom is transferred to a site in which the vibrational frequencies are significantly increased, and in particular when H(D) is transferred from a metal to a carbon atom [7]. In the case of C–H/D elimination, inverse KIEs seem to imply endothermic eliminations, presumably since significant C–H/D bond formation is found in a later transition state ([7]; for examples of normal KIEs for reductive elimination of C–H(D) bonds see [8]). Jones has measured a KIE of 0.52 for C–H elimination of benzene for Cp^*RhL (to give the η^2 -benzene complex) [7]. In the particular case of C_6H_{12}/C_6D_{12} elimination from a d^8 metal center, Bergman has observed an inverse KIE of 0.7 for elimination from $Cp^*IrL(H/D)(cyclohexyl)$ [9]. Thus, taken together, these results strongly suggest that: (i) CO inhibition occurs via attack on an alkane adduct; (ii) the adduct is specifically an oxidative addition product, rather than a loosely bound solvated or σ -bound species — indeed, Moore and Bergman have shown that (for reasons as yet unclear) C_6D_{12} coordinates considerably *more* strongly to the Rh(I) center of $Cp^*Rh(CO)$ (ca. 1.0 kcal/mol) [10] and thus the kinetic isotope effect for dissociation of the σ -bound alkane would presumably be normal.

Independent of the isotope effect, it may be noted that loss of alkane is much slower than CO addition (Eq. (6)) in the saturation regime ($> ca. 400$ torr, corresponding to ca. 4 mM [CO]).² Based on diffusion limitations for CO addition, an upper limit for the rate of alkane exchange can be estimated as ca. $10^6 s^{-1}$; this implies an activation barrier ($\Delta G^\ddagger$) of ca. 10 kcal/mol for alkane exchange which seems more consistent with an alkyl hydride than with a σ -bound or solvated species.

A 'qualitative' understanding of the effect that varying [CO] has on product selectivity is most easily achieved if we posit that product formation occurs via a rate-determining irreversible reaction of the alkyl hydride which occurs with rate constant k_4 . (For purposes of this discussion we will assume that this step is β -hydrogen elimination; however, it can also be a composite reaction such as reversible β -hydrogen elimination followed by irreversible loss of olefin, with an *overall* rate constant of k_4 .) Eq. (12) and Eq. (13) then reduce to Eq. (14) and Eq. (15), respectively (by assuming $k_{-4} \ll k_5$) in the case of 1:1 solvent mixtures.

² The solubility of CO in alkanes is estimated to be approximately equal to that in benzene; under 800 torr [CO] = 0.0072 M: see [11].

$$\frac{d[\text{CHE-d}_{10}]/dt}{d[\text{CHE-h}_{10}]/dt} = \frac{K_{2a}k_{4a}}{K_2k_4} = 0.10 \quad (\text{no CO}) \quad (14)$$

$$\frac{d[\text{CHE-d}_{10}]/dt}{d[\text{CHE-h}_{10}]/dt} = \frac{k_{2a}k_{4a}}{k_2k_4} = 0.24 \quad (\text{high CO pressure}) \quad (15)$$

In the low-[CO] limit, the alkyl hydride isotopomers exist in a pre-equilibrium and the product ratio reflects the equilibrium constant (K_{2a}/K_2) and the ratio of rates of β -H elimination (k_{4a}/k_4). In the high-[CO] limit, the alkyl hydride most frequently reacts with CO (unproductively); elimination of alkane is kinetically insignificant. In this case, the product ratio reflects the relative rates of C–H addition (k_{2a}/k_2) and the relative rates of β -H elimination (k_{4a}/k_4). Thus both limits are dependent upon the relative rates of β -H elimination; however, in the high-pressure case β -H elimination is predominantly in competition with CO addition, while in the low-pressure case it occurs predominantly in competition with elimination or exchange of alkane.

2.3. Conclusions

Varying CO pressure significantly affects the intermolecular selectivity (cyclooctane/cyclohexane or $\text{C}_6\text{D}_{12}/\text{C}_6\text{H}_{12}$) of **1**-catalyzed alkane dehydrogenation, with saturation being observed at ca. 400 torr CO. In conjunction with previous mechanistic studies, this effect can only be explained by a mechanism in which CO attacks the respective alkane adducts — even if CO addition to the different adducts is assumed to occur at equal rates (as is the case in the $\text{C}_6\text{D}_{12}/\text{C}_6\text{H}_{12}$ competition). An inverse isotope effect for loss of alkane from the adduct is calculated, $k_{h-12}/k_{d-12} = 0.42$; this strongly suggests that the adducts are alkyl hydrides (deuterides) rather than solvated or σ -bound species. Since the reaction of CO with other species such as solvated or σ -bound RhL_2Cl does not occur to a kinetically significant extent, it may be inferred that such species are not present in significant concentration relative to the alkyl hydrides. This implies that formation of the alkyl hydrides, i.e. oxidative addition to the RhL_2Cl photoproduct, is both kinetically very facile and thermodynamically very favorable.

3. Experimental

3.1. General procedures

All samples were prepared under an argon atmosphere in a Vacuum Atmospheres Dry-Lab glovebox. Solvents were distilled under vacuum from NaK alloy. $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ (**1**) was prepared as described previously [4]. Gas chromatographic analyses for all experi-

ments were performed with a temperature-programmed Varian 3400 using a 50-m HP-1 (cross-linked methylsilicone gum phase) capillary column and a flame ionization detector. Authentic cyclooctene and cyclohexene were used to generate calibration curves which encompassed the experimental concentration range. Baseline separation of the cyclohexane isotopomers was achieved; the identity of C_6D_{10} was confirmed by comparison with authentic C_6D_{10} generated from dedeuterogenation of C_6D_{12} . Irradiations were conducted using a 500 W Hg-arc Oriel lamp, and the desired wavelengths were achieved using filters obtained from FJ Gray (Corning 7-83 for 366 nm and 0-56 for $\lambda > 280$ nm).

3.2. Typical photolysis conditions

Stock solutions of 2.0 mM **1** were prepared in cyclooctane, cyclohexane, and d_{12} -cyclohexane. In general, 1.5-ml samples were prepared using the appropriate mixture of stock solutions. The samples were placed in a quartz cuvette sealed to a ballast used to maintain constant partial gas pressures and equipped with ports for attachment to a vacuum line and for removal of microliter samples for GC analysis. The samples were placed under a total pressure of 800 torr (mixtures of Ar and CO), and then irradiated at 50°C. The samples were then analyzed at various times by GC for alkene formation. Product ratios COE:CHE and CHE- d_{10} :CHE- h_{10} were found to remain constant with time.

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