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Phenomenological Aspects of Homogeneous Catalysis. The Case of Equilibrium-Controlled Precursor Conversion

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The homogeneous catalytic hydroformylation of cyclohexene was performed, starting with $Rh_4(CO)_{12}$ as catalyst precursor in *n*-hexane as solvent under the reaction conditions $T = 283$–303 K, $P_{H_2} = 1.0$–4.0 MPa, $P_{CO} = 4.0$–8.0 MPa, $[Rh_4(CO)_{12}]_0 = (5$–$21) \times 10^{-6}$ mole fraction, and $[C_6H_{10}]_0 = 0.05$–0.18 mole fraction. The time-dependent concentrations of the precursor $Rh_4(CO)_{12}$, the intermediate $C_6H_{11}CORh(CO)_4$, and the organic product $C_6H_{11}CHO$ were measured under isobaric and isothermal conditions using in situ high-pressure infrared spectroscopy. The metal carbonyl $Rh_2(CO)_8$ was also detected during the hydroformylation experiments. Complete conversion of the precursor $Rh_4(CO)_{12}$ to the intermediate $C_6H_{11}CORh(CO)_4$ was not observed during the 18-h experiments. After approximately 30 min of reaction, an apparent pseudo steady state was achieved between the precursor $Rh_4(CO)_{12}$ and the intermediate $C_6H_{11}CORh(CO)_4$. Regression of the experimental concentration data gave the relationship $[C_6H_{11}CORh(CO)_4]_{ss} = (K_{eq}^{0.25}k_2/k_{1obs})[Rh_4(CO)_{12}]_{ss}^{0.3}[CO]^{1.1}[H_2]^{-0.3}[C_6H_{10}]^{0.9}$, with the apparent temperature dependence $\Delta_{ss}H_x = -4.7 \pm 0.3$ kJ/mol (-1.1 ± 0.1 kcal/mol) and $\Delta_{ss}S_x = -27.6 \pm 0.7$ J/(mol K) (-6.6 ± 0.2 cal/(mol K)). The results are consistent with (I) an equilibrium between the precursor $Rh_4(CO)_{12}$, H_2, and an unobservable intermediate $\{HRh(CO)_3\}$ and (II) the existence of a pseudo steady state between $\{HRh(CO)_3\}$ and the observed intermediate $C_6H_{11}CORh(CO)_4$. The present catalytic system represents a case of equilibrium-controlled precursor conversion. The rate of hydroformylation was found to be proportional to the pseudo-steady-state concentrations of $C_6H_{11}CORh(CO)_4$ in each experiment. Regression of the experimental rate data provided the expression $d[C_6H_{11}CHO]/dt = k_{1obs}[C_6H_{11}CORh(CO)_4]_{ss}^1[CO]^{-1.1}[H_2]^1[C_6H_{10}]^{0.1}$, with the apparent activation parameters $\Delta^{\ddagger}H_x = 84.6 \pm 5.0$ kJ/mol (20.3 ± 1.2 kcal/mol) and $\Delta^{\ddagger}S_x = -8.7 \pm 17$ J/(mol K) (2.1 ± 4.1 cal/(mol K)). The reaction orders and activation parameters are consistent with (I) an equilibrium between the intermediate $C_6H_{11}CORh(CO)_4$, CO, and a coordinatively unsaturated species $\{C_6H_{11}CORh(CO)_3\}$ and (II) a rate-limiting step involving the oxidative addition of molecular hydrogen to $\{C_6H_{11}CORh(CO)_3\}$ to yield $C_6H_{11}CHO$ and the highly reactive metal carbonyl hydride $\{HRh(CO)_3\}$.

Introduction

In its unmodified forms, i.e. starting with $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ as catalyst precursors,[1] rhodium effects the selective hydroformylation of a wide variety of alkenes.[2] The reactivity pattern for unfunctionalized alkenes follows the order styrene > linear α > linear internal > branched > cyclic.[3] Many cyclic alkenes, including cyclohexene, show exceptionally low reaction rates. However, the hydroformylation of cyclohexene results in just one aldehyde, namely cyclohexanecarboxaldehyde,[4] with negligible hydrogenation to cyclohexane (eq 1). Thus, cyclohexene has been the alkene of choice in numerous mechanistic studies.[5]

$$C_6H_{10} + H_2 + CO \rightarrow C_6H_{11}CHO \qquad (1)$$

Markó et al. have studied the reactivity of a number of unfunctionalized alkenes,[3] including cyclohexene.[6] With most alkenes, the rate of hydroformylation is known to be proportional to the product $[Rh_4(CO)_{12}]_0^1[CO]^{-1}[H_2]^1[\text{alkene}]^0$. However, the hydroformylation of cyclohexene at 348 K, and starting with $Rh_4(CO)_{12}$ as catalyst precursor, results in an entirely different rate expression (eq 2). This led these authors to suggest that an equilibrium exists between the catalyst precursor and a coordinatively unsaturated species $\{HRh(CO)_3\}$. Further support for this assertion comes from the hydroformylation

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[1] (a) The term *catalyst precursor*, or simply *precursor*, will be adopted to describe *a metal complex which under reaction conditions gives rise to a closed sequence(s) of organometallic intermediates and thereby effects the catalyzed transformation of reagents to products.* (b) This usage is consistent with that found in: Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Eng.* **1983**, *22*, 135.

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[3] (a) Markó, L. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1974; Vol. 1. (b) Heil, B.; Markó, L. *Chem. Ber.* **1969**, *102*, 2238. (c) Heil, B.; Markó, L. *Chem. Ber.* **1968**, *101*, 2209.

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[5] Concerning the hydroformylation of cyclohexene starting with unmodified rhodium carbonyls, see: (a) Gankin, V. Yu.; Genender, L. S.; Rudkovskii, D. M. *J. Appl. Chem. USSR* (*Engl. Transl.*) **1967**, *40*, 1948. (b) Imyanitov, N. S.; Rudkovskii, D. M. *J. Appl. Chem. USSR* (*Engl. Transl.*) **1967**, *40*, 1956. Concerning the hydroformylation of cyclohexene starting with phosphine-modified rhodium carbonyls, see: (c) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133. Concerning the hydroformylation of cyclohexene starting with unmodified cobalt carbonyls see: (d) Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 3041. (e) Natta, G.; Ercoli, R.; Castellano, S. *Chim. Ind.* (*Milan*) **1955**, *37*, 6.

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$$d[C_6H_{11}CHO]/dt = k[Rh_4(CO)_{12}]_0^{0.25}[CO]^0[H_2]^{0.5}[C_6H_{10}]^1 \quad (2)$$

of cyclohexene starting with $Rh_6(CO)_{16}$ as catalyst precursor.[7] Unusually long induction periods have sometimes been observed when using cyclohexene.

In a later investigation carried out at 398 K, yet another rate expression was obtained for the hydroformylation of cyclohexene (eq 3).[8] This result led to the suggestion that the transformation of cyclohexene to cyclohexanecarboxaldehyde occurs on a unicyclic sequence of tetranuclear rhodium intermediates, specifically the four-cycle $\{Rh_4(CO)_{12} \rightarrow H_2Rh_4(CO)_{12} \rightarrow C_6H_{11}(H)Rh_4(CO)_{12} \rightarrow C_6H_{11}CO(H)Rh_4(CO)_{12}\}$, where the critical step is the activation of molecular hydrogen and the formation of the intermediate $H_2Rh_4(CO)_{12}$. In other words, it was concluded that fragmentation of $Rh_4(CO)_{12}$ to lower nuclearity species does not occur and that the hydroformylation of cyclohexene is due to "cluster catalysis".[9]

$$d[C_6H_{11}CHO]/dt = k[Rh_4(CO)_{12}]_0^1[CO]^1[H_2]^1[C_6H_{10}]^1 \quad (3)$$

In situ spectroscopic methods have been successfully applied to unmodified rhodium catalyzed hydroformylation reactions on several occasions. For example, the intermediate $(CH_3)_3CCH_2CH_2CORh(CO)_4$ was identified using in situ high-pressure IR, as the only observable intermediate during the hydroformylation of 3,3-dimethylbut-1-ene starting with both $CoRh(CO)_7$ and $Rh_4(CO)_{12}$ as catalyst precursors.[10,11] $(CH_3)_3CCH_2CH_2CORh(CO)_4$ was subsequently observed during hydroformylations starting with $Rh_6(CO)_{16}$, $Rh_2(CO)_4Cl_2$, $RhCl_3{\cdot}2H_2O$, and $Co_2Rh_2(CO)_{12}$ as well.[12a] Other acylrhodium tetracarbonyls $RCORh(CO)_4$ have now been spectroscopically identified starting with ethylene, 1-hexene, 1-octene, cyclopentene, cycloheptene, cyclooctene, methylenecyclopentane, methylenecyclohexane, and bicyclo[2.2.1]hept-2-ene.[12b,c]

Concerning the kinetics of such reactions, the complex time dependence of 3,3-dimethylbut-1-ene hydroformylation starting with $Rh_4(CO)_{12}$ has been successfully treated.[13] In that study, *quantitative* conversion of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ was observed by in situ IR, and the rate expressions for both the induction period and the turnover frequency of the catalytic cycle were obtained. It was concluded that the classic mechanistic picture of the hydroformylation reaction is indeed valid, namely that the rate-limiting step involves the hydrogenolysis of $RCORh(CO)_4$ (eqs 4 and 5).

$$RCORh(CO)_4 \rightleftharpoons CO + \{RCORh(CO)_3\} \quad (4)$$

$$\{RCORh(CO)_3\} + H_2 \rightarrow RCHO + \{HRh(CO)_3\} \quad (5)$$

Given the anomalous reactivity of cyclohexene compared to other unfunctionalized alkenes and given the difficulty in obtaining consistent experimental results as shown in previous studies, the hydroformylation of cyclohexene starting with $Rh_4(CO)_{12}$ was reinvestigated using a combined spectroscopic and numerical approach. In the following, in situ spectroscopic measurements as well as turnover frequencies and reaction orders are reported.

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern, Switzerland) or argon (99.998%, Pan Gas) atmosphere using standard Schlenk techniques.[14] $Rh_4(CO)_{12}$ was purchased from Strem Chemicals (Bischheim, France) and was used as obtained. Puriss quality *n*-hexane (Fluka AG, Buchs, Switzerland) was refluxed from sodium potassium alloy under nitrogen. Puriss quality 1,3-cyclohexadiene (Fluka AG) and cyclohexane carboxaldehyde (Merck, Darmstadt, Germany) were used as obtained. Reactions were carried out with carbon monoxide 99.997% (Messer Griesheim GmbH, Duisburg, Germany) and hydrogen 99.999% (Pan Gas).

The Puriss quality cyclohexene obtained for this study (Fluka AG) contained 0.2% cyclohexane and 0.2% 1,3-cyclohexadiene as impurities, as determined by GC using a 10-m capillary column with 23% SP1700 packing (Supelco SA, Gland, Switzerland). The cyclohexene was refluxed with 2 equiv of maleic anhydride until no 1,3-cyclohexadiene could be detected by gas chromatography.[15] The resulting cyclohexene was washed repeatedly with distilled water, passed over 4-Å molecular sieves, distilled from CaH_2, and stored under nitrogen at 273 K. Trace impurities of 1,3-cyclohexadiene led to irreproducible and/or intractable kinetic results. In addition to ν_{CO} bands belonging to $C_6H_{11}CORh(CO)_4$, new bands appeared in the in situ infrared spectra taken during the active hydroformylation experiments involving trace quantities of 1,3-cyclohexadiene.

Equipment. Kinetic studies were performed in a 1.5-L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) which was connected to a high-pressure infrared cell. The autoclave (P_{max} = 22.5 MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie, PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK30, Orlita AG, Giessen, Germany) with a maximum rating of 32.5 MPa and 3-L/h flow rate was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via jacketed $^1/_8$-in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, autoclave, transfer lines, and infrared cell, was cooled using a Lauda RX20 (Königshofen, Germany) cryostat, and could be maintained isothermally (ΔT = 0.5 °C) in the range −20 to +40 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with PT-100 thermoresistors. The necessary connections to vacuum and gases were made with $^1/_4$-in. (SS316) high-pressure tubing (Autoclave Engineers), and 5.00-, 10.00-, and 20.00-MPa piezocrystals were used for pressure measurements (Keller AG, Winterthur, Switzerland). The piezocrystals were periodically calibrated on a Haenni PDG 022 calibration bench (Stuttgart, Germany). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

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[7] In the case of $Rh_6(CO)_{16}$ as precursor, the kinetics of the hydroformylation of cyclohexene gives $d[C_6H_{10}]/dt \propto [Rh_6(CO)_{16}]_0^{1/6}$. (a) Reference 6. (b) Toros, S. *Magy. Kem. Lapja* **1974**, *29*, 543; *Chem. Abstr.* **1975**, *83*, 177 870.

[8] Rosas, N.; Marquez, C.; Hernandez, H.; Gomez, R. *J. Mol. Catal.* **1988**, *48*, 59.

[9] (a) Cluster catalysis can be defined to be *the catalytic transformation of reagents to products via a closed unicyclic sequence of organometallic intermediates, all having one and the same nuclearity* ($m \geq 2$). (b) For general discussions of "cluster catalysis" see: (c) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* **1975**, *44*, 43. (d) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. (e) Ugo, R. *Catal. Rev.* **1975**, *11*, 225. (f) Muetterities, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

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The high-pressure infrared cell was constructed at the ETH-Zürich of SS316 steel and could be heated or cooled. The CaF_2 single crystal windows (Korth Monokristalle, Kiel, Germany) had dimensions of 40-mm diameter by 15-mm thickness. Two sets of Viton and silicone gaskets provided sealing, and the Teflon spacers were used between the windows. The construction of the flow through cell[16a] is a variation on a design due to Noack[16b] and differs in some respects from other high-pressure infrared cells described in the literature (for a review, see Whyman[16g]). The high-pressure cell was situated in a Perkin-Elmer PE983 infrared spectrophotometer equipped with a Model 3600G data station. Details of the equipment and IR cell can be found elsewhere.[10a]

Spectroscopic Aspects. The infrared absorbance spectrum of the solvent *n*-hexane,[17a,d] the reagent C_6H_{10},[17b,e] and the product $C_6H_{11}CHO$[17c] are all well documented. The absorptivity at 293 K for *n*-hexane, for the maximum centered at 2373 cm^{-1}, with minima at 2400 and 2318 cm^{-1}, is $\epsilon_{ane} = 0.248$ L/(mol cm). The absorptivity at 293 K for cyclohexene at 2373 cm^{-1}, with minima at 2400 and 2318 cm^{-1}, is $\epsilon_{ene} = 0.212$ L/(mol cm). The arithmetic mean absorptivity for mixtures containing n_{ane} moles of *n*-hexane and n_{ene} moles of cyclohexene was calculated from eq 6.

$$\epsilon_{2373} = (\epsilon_{ene}n_{ene} + \epsilon_{ane}n_{ane})/(n_{ene} + n_{ane}) \qquad (6)$$

The organic product $C_6H_{11}CHO$ has a prominent absorbance maximum at 1734 cm^{-1} due to the C=O stretching mode.[18c] The absorptivity, as determined in the limit of infinite dilution in *n*-hexane, was $\epsilon_{1734} = 372$ L/(mol cm).

The tetranuclear carbonyl $Rh_4(CO)_{12}$ has absorbance maxima at 2074, 2068, 2061, 2043, and 1885 cm^{-1} in the infrared.[19a,b] The determined absorptivity of $Rh_4(CO)_{12}$ at infinite dilution in pure *n*-hexane at 1885 cm^{-1} (bridging CO) was $\epsilon_{1885} = 9800$ L/(mol cm).[13]

The intermediate $RCORh(CO)_4$ has absorbance maxima at 2111, 2065, 2039, 2020, and 1698 cm^{-1} in *n*-hexane.[10,11] Given the low conversions of $Rh_4(CO)_{12}$ to $C_6H_{11}CORh(CO)_4$ observed in the present study, calibrations for the absorptivity at 2020 cm^{-1} were not performed. Instead, the absorptivity of $(CH_3)_3CCH_2CH_2CORh(CO)_4$ in *n*-hexane was taken: $\epsilon_{2020} = 4150$ L/(mol cm).[12a] With the aforementioned absorptivities, excellent rhodium mass balances were obtained for the duration of all experiments conducted at $T \leq 298$ K (less than 6% variation from the nominal value). The experiment at 303 K showed a 12% variation. It is known that the absorptivities ϵ_{CO} of metal carbonyls $R{-}R'{-}M(CO)_x$ are only marginally affected by changes in substituents R.[20]

The concentrations of $Rh_4(CO)_{12}$, $C_6H_{11}CORh(CO)_4$, and $C_6H_{11}CHO$ were calculated during the hydroformylation experiments from measurements of in situ absorbance using the dimensionless Lambert–Beer law presented in eq 7.[21] The term

$$x_i = x_{C_6}(A_i\epsilon_{2373})/(A_{2373}\epsilon_i) \qquad (7)$$

x_{C_6} is the sum total of the mole fractions of both hydrocarbons, namely *n*-hexane and cyclohexene, at the initial reaction conditions (eq 8). Less than 4.1% conversion of C_6H_{10} to $C_6H_{11}CHO$ occurred in any experiment.

$$x_{C_6} = (n_{ane} + n_{ene})_0/(n_{ane} + n_{ene} + n_{CO} + n_{H_2})_0 \qquad (8)$$

Kinetic Studies. $Rh_4(CO)_{12}$ was dissolved in 200 mL of n-hexane (1.51 mol) in a Schlenk tube under a nitrogen atmosphere, cyclohexene was added, and the solution was transferred into the evacuated and thermostated autoclave. Depending on the system temperature, the total pressure in the autoclave was $P_T = 0.01{-}0.03$ MPa, the vapor pressure of *n*-hexane plus a low partial pressure of nitrogen. With stirring (200 rpm), carbon monoxide (4.0–8.0 MPa) was added to the system. The high-pressure membrane pump continuously circulated the *n*-hexane solution from the autoclave to the high-pressure infrared cell and back to the autoclave. At a time $t = 0$, a program was executed to record spectra every 15 or 30 min. Initial in situ infrared spectra were then taken from 2500 to 1600 cm^{-1}. The initial spectra show that the reagents $Rh_4(CO)_{12}$, dissolved CO (2300–2000 cm^{-1}), and C_6H_{10} (1654 cm^{-1})[18d] can be clearly identified. Little, if any additional noise could be identified in the in situ spectra as the solution was pumped (10 cm/s) through the high-pressure infrared cell. After the initial spectra were recorded, hydrogen (1.0–4.0 MPa) was added to the system. After 18 h, the experiments were stopped and the spectra were analyzed off-line.

Five sets of experiments were performed. In each set, one experimental parameter was systematically varied while the remaining variables were held essentially constant. In this manner, variations in the concentrations of initial $Rh_4(CO)_{12}$ and initial cyclohexene, dissolved hydrogen, and dissolved carbon monoxide and variations in temperature were studied. The initial reaction conditions of the "reference" experiment were 17.2×10^{-6} mole fraction of $Rh_4(CO)_{12}$, 30 mL of cyclohexene (0.144 mole fraction), 2.0 MPa of hydrogen (0.018 mole fraction), and 6.0 MPa of carbon monoxide (0.095 mole fraction) in *n*-hexane at 293 K. The reproducibility of experiments conducted at the reference reaction conditions was excellent. Blank experiments, conducted at the reference reaction conditions, but in the absence of $Rh_4(CO)_{12}$ showed a negligible 4% residual activity as compared with the reference experiment.

The present hydroformylation reactions were performed under negligible gas–liquid mass transfer resistance. The experimentally measured overall mass transfer coefficients K_La for hydrogen and carbon monoxide into *n*-hexane at 200 rpm were approximately 0.1 and 0.06 s^{-1}, respectively, as determined using the method of Deimling.[22a] Since the maximum observed rate of hydroformylation in this study was 9×10^{-8} mol s^{-1}, all experiments belong to the category of infinitely slow reaction with respect to gas–liquid mass transfer (the kinetic regime, Hatta category H).[22b] The liquid phase of each experiment became essentially saturated with dissolved CO and H_2 in the first 60 s. Mass transfer effects are known to severely complicate the interpretation of kinetic data from hydroformylation reactions.[22c]

In any single 18-h kinetic experiment, less than 0.012-mol conversion of C_6H_{10} to $C_6H_{11}CHO$ occurred. The partial pressures of hydrogen and carbon monoxide in the closed-batch autoclave changed less than 1–2% during the 18-h experiments. This partial pressure change was considered negligible, and therefore, the

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(20) In the series $R{-}C_6H_4COOCH_3Cr(CO)_3$ (R = *m*-$COOCH_3$, *p*-$COOCH_3$, *o*-Cl, *m*-Cl, *p*-Cl, H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *o*-CH_3, *o*-OCH_3), the experimentally measured absorptivities were $\epsilon_{A1} = 6800{-}8000$ L/(mol cm) and $\epsilon_E = 3250{-}4100$ L/(mol cm). Klopman, G.; Noack, K. *Inorg. Chem.* **1968**, *7*, 579.

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liquid phase concentrations of the two gaseous components were treated as constants for the duration of each experiment.

The rates of reaction, for the transformation of cyclohexene to cyclohexanecarboxaldehyde were calculated using the finite difference eq 9. This expression provides a numerical value for

$$(\mathrm{d}[\mathrm{C_6H_{11}CHO}]/\mathrm{d}t)_t = ([\mathrm{C_6H_{11}CHO}]_{t+1} - [\mathrm{C_6H_{11}CHO}]_{t-1})/2\Delta t \quad (9)$$

the rate of hydroformylation at a time t, based on the measured in situ concentrations of $C_6H_{11}CHO$ at times $t - 1$ and $t + 1$. The time interval between t and $t - 1$ or $t + 1$ was 15 min for $t \leq 90$ min and 30 min thereafter. This central difference expression was chosen since it provides an accurate approximation of derivatives from sets of smooth monotonically increasing or decreasing experimental data.[23]

Solubilities. Solubility data for hydrogen[24a] and carbon monoxide[24b] in n-hexane are available from the literature. The Henry constants were calculated using eqs 10 and 11, respectively,

$$H_{\mathrm{H_2}}(P,T) = P_{\mathrm{sat}} \exp(-4.96 + 4050/T) \times \exp(v_{\mathrm{CO}}(P - P_0)/RT) \quad (10)$$

$$H_{\mathrm{CO}}(P,T) = P_{\mathrm{sat}} \exp(-5.05 + 3880/T) \times \exp(v_{\mathrm{H_2}}(P - P_0)/RT) \quad (11)$$

where the temperature T is in Kelvin and where P_{sat} is the saturated vapor pressure of the n-hexane.[25] The derivation of the temperature-dependent form used can be found in the literature.[26] These equations are strictly valid only for pure hexane. The Krichevsky–Kasarnovsky correction for total pressure effects on the Henry constants has been included, where P_0 is the standard reference pressure 0.1 MPa.[27] The partial molar volumes of H_2 and CO in aliphatic hydrocarbons including n-hexane are $v_{\mathrm{H_2}} = 43$ mL/mol,[28] and $v_{\mathrm{CO}} = 52$ mL/mol.[29] Finally, both dissolved hydrogen and dissolved carbon monoxide were considered to be ideal solutes. No mixing rules were invoked in order to compensate for nonideality in the two-phase system, and the Krichevsky–Ilinskaya correction was not employed.[30]

Kinetic Results

Precursor Concentration. The initial concentration of the precursor $Rh_4(CO)_{12}$ was systematically varied in four hydroformylation experiments performed at 293 K, 0.144 mole fraction of cyclohexene, 2.0 MPa of hydrogen (0.018 mole fraction), and 6.0 MPa of carbon monoxide (0.095 mole fraction). The initial concentrations of $Rh_4(CO)_{12}$, based on in situ IR spectroscopic measurements, were $[Rh_4(CO)_{12}]_0 = 5.3 \times 10^{-6}, 9.7 \times 10^{-6}, 17.2 \times 10^{-6}$, and 20.7×10^{-6} mole fraction.

In situ infrared spectra of the solution, under 6.0 MPa of CO and before the addition of hydrogen, clearly showed the characteristic absorbance of the precursor $Rh_4(CO)_{12}$, the alkene C_6H_{10}, and dissolved CO, in addition to the solvent n-hexane. The cluster $Rh_6(CO)_{16}$, a common impurity in $Rh_4(CO)_{12}$, was apparently absent from solution, as indicated by the lack of absorbance maxima at ν_{CO} = 2105, 2070 (s), 2047, 2040, 2022, 2020, 1833, and 1793 (s) cm^{-1}.[31] However, the presence of $Rh_2(CO)_8$ was clearly indicated by the characteristic absorbances at ν_{CO} = 2086, 2061, 1860, and 1845 cm^{-1}.[32] The dinuclear carbonyl is known to undergo rapid equilibration with $Rh_4(CO)_{12}$ in n-hexane solution (eq 12) in the presence of

$$\mathrm{Rh_4(CO)_{12} + 4CO \rightleftharpoons 2Rh_2(CO)_8} \quad (12)$$

high P_{CO} and at temperatures as low as 253 K.[33a] Though detectable, the extent of cluster fragmentation and conversion to $Rh_2(CO)_8$ was always less than 2–3% in these and in all subsequent kinetic experiments.

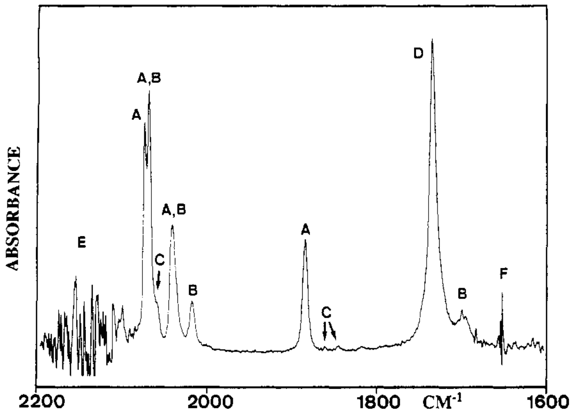

Figure 1. In situ high-pressure infrared spectrum of a hydroformylation solution after 480 min of reaction (n-hexane, cyclohexene, and CO subtraction). Conditions: $[Rh_4(CO)_{12}]_0 = 17.3 \times 10^{-6}$ mole fraction, $[C_6H_{10}]_0 = 0.144$ mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa), in n-hexane at 293 K. Key: (A) $Rh_4(CO)_{12}$ (14.2×10^{-6} mole fraction), (B) $C_6H_{11}CORh(CO)_4$ (13.7×10^{-6} mole fraction), (C) $Rh_2(CO)_8$, (D) cyclohexanecarboxaldehyde (9.1×10^{-4} mole fraction), (E) noise in the dissolved CO region, (F) noise in the cyclohexene ($\nu_{\mathrm{C=C}}$ 1654 cm^{-1}) region. The cell width is approximately 0.5 mm.

Upon addition of hydrogen, absorbance maxima due to the intermediate $C_6H_{11}CORh(CO)_4$ at ν_{CO} = 2111, 2065, 2040, 2020, and 1695 cm^{-1}, and the organic product $C_6H_{11}CHO$ at 1734 cm^{-1} slowly appeared. Total conversion of the precursor $Rh_4(CO)_{12}$ never occurred in the 18-h experiments, and $Rh_2(CO)_8$ continued to exist in solution at observable concentrations. No new and additional ν_{CO} absorbance maxima appeared. A typical in situ infrared difference spectrum, obtained by n-hexane/cyclohexene/CO subtraction and taken under 8.0-MPa total pressure is shown in Figure 1. In this spectrum, as well as all other spectra taken during kinetic runs with n-hexane as solvent, good baselines and low noise levels ($<10^{-2}$ absorbance units) were observed in the important metal–carbonyl region of the IR spectra from 2075 to 1800 cm^{-1}.

The concentration of the intermediate $C_6H_{11}CORh(CO)_4$ as a function of time and as a function of the initial concentration of $Rh_4(CO)_{12}$ for the four experiments is shown in Figure 2. After a relatively short 30-min period, the concentrations of the intermediate $C_6H_{11}CORh(CO)_4$ become essentially time-independent for the remaining 1000 min of each experiment. This time-independent period corresponds to a pseudo steady state between the

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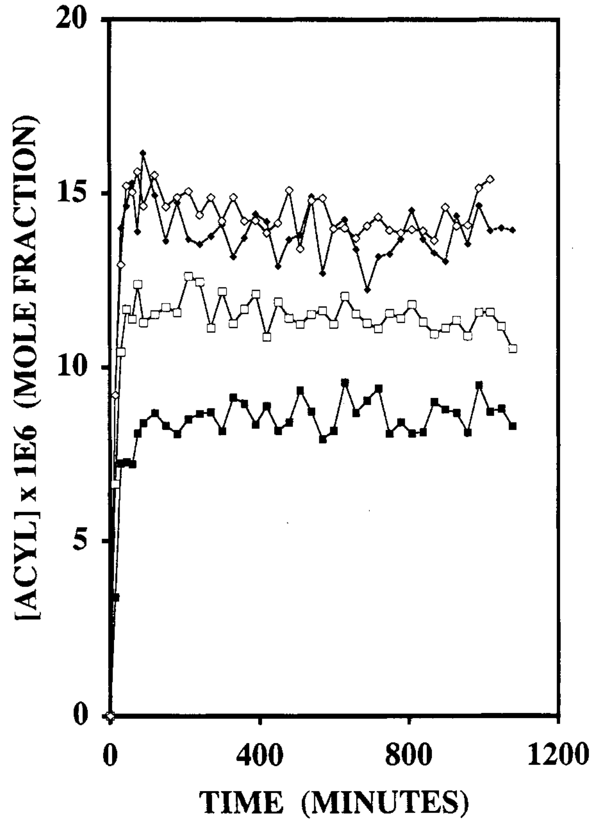

Figure 2. Effect of the initial $Rh_4(CO)_{12}$ concentration on the formation of $C_6H_{11}CORh(CO)_4$ as a function of time. Conditions: $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) $[Rh_4(CO)_{12}]_0 = 5.3 \times 10^{-6}$, (□) $[Rh_4(CO)_{12}]_0 = 9.7 \times 10^{-6}$, (♦) $[Rh_4(CO)_{12}]_0 = 17.2 \times 10^{-6}$, (◇) $[Rh_4(CO)_{12}]_0 = 20.7 \times 10^{-6}$ mole fraction.

precursor $Rh_4(CO)_{12}$ and the intermediate $C_6H_{11}CORh(CO)_4$. Increased initial concentrations of $Rh_4(CO)_{12}$ lead to increased pseudo-steady-state concentrations of $C_6H_{11}CORh(CO)_4$, but these two quantities are not proportional.

Figure 2 suggests that the absolute error associated with the measurements of these pseudo-steady-state concentrations is very low, i.e., on the order of 1×10^{-6} mole fraction. Indeed, regressions of $[C_6H_{11}CORh(CO)_4]_{ss}$ after the 30-min induction period gave $[C_6H_{11}CORh(CO)_4]_{ss}$ = $(8.5 \pm 0.6) \times 10^{-6}$, $(11.5 \pm 0.5) \times 10^{-6}$, $(13.9 \pm 0.7) \times 10^{-6}$, and $(14.4 \pm 0.06) \times 10^{-6}$ in the experiments starting with $[Rh_4(CO)_{12}]_0 = 5.3 \times 10^{-6}, 9.7 \times 10^{-6}, 17.2 \times 10^{-6}$, and 20.7×10^{-6} mole fraction.[34] Further, independent measurements of $[Rh_4(CO)_{12}]_{ss}$ gave $(3.2 \pm 0.2) \times 10^{-6}$, $(7.4 \pm 0.2) \times 10^{-6}$, $(14.0 \pm 0.3) \times 10^{-6}$, and $(17.6 \pm 0.3) \times 10^{-6}$ respectively. Therefore, excellent mass balances over rhodium were obtained. Only 40.1, 24.0, 18.6, and 15.2% conversion of $Rh_4(CO)_{12}$ have occurred during the hydroformylation experiments.[35]

Since (I) $C_6H_{11}CORh(CO)_4$ is the only observable intermediate, (II) the spectroscopic measurements are of high accuracy and good quality, and (III) excellent mass balances on rhodium are obtained, then the remaining pseudo-steady-state intermediate concentrations in the system can be assumed to be very low. This suggests the validity of the following approximation (eq 13), where the summation extends over all organometallic intermediates N_i in solution.

$$[C_6H_{11}CORh(CO)_4]_{ss} \approx \sum[N_i]_{ss} \qquad (13)$$

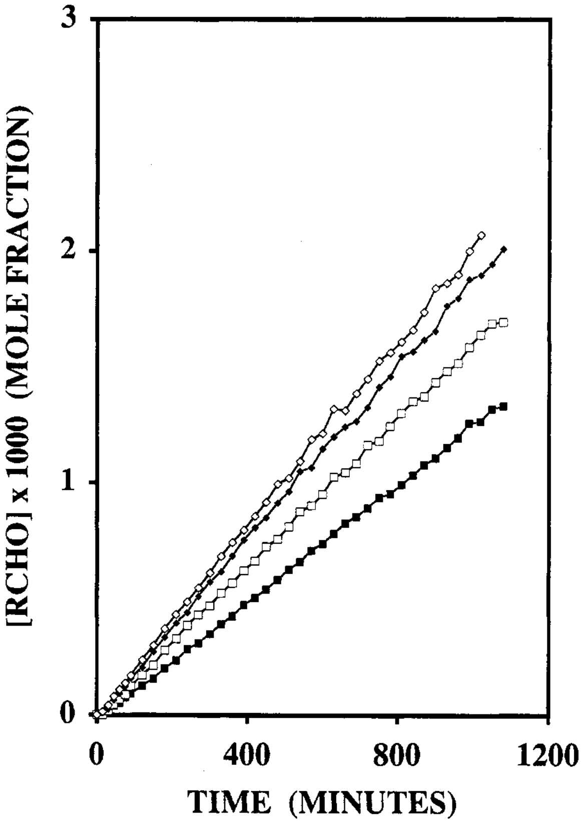

Figure 3. Effect of the initial $Rh_4(CO)_{12}$ concentration on the formation of $C_6H_{11}CHO$ as a function of time. Conditions: $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) $[Rh_4(CO)_{12}]_0 = 5.3 \times 10^{-6}$, (□) $[Rh_4(CO)_{12}]_0 = 9.7 \times 10^{-6}$, (♦) $[Rh_4(CO)_{12}]_0 = 17.2 \times 10^{-6}$, (◇) $[Rh_4(CO)_{12}]_0 = 20.7 \times 10^{-6}$ mole fraction.

Equation 14 was used to correlate the pseudo-steady-state concentrations of the precursor $Rh_4(CO)_{12}$ and the intermediate $C_6H_{11}CORh(CO)_4$ (see Discussion). The exponent for the precursor $Rh_4(CO)_{12}$ was $\alpha_p = 0.32 \pm 0.02$ as determined by regression of the mean concentrations.[36]

$$[C_6H_{11}CORh(CO)_4]_{ss} = \Phi[Rh_4(CO)_{12}]_{ss}^{\alpha_p}\prod x_i^{\alpha_i} \qquad (14)$$

The time-dependent concentrations of the organic product $C_6H_{11}CHO$ for the four experiments, are shown in Figure 3. After the first 30 min, the concentrations of $C_6H_{11}CHO$ become linear functions of time. There is very little scatter in the in situ measured concentration data.

The final conversions of C_6H_{10} after 18 h were 0.92, 1.17, 1.38, and 1.44% at $[Rh_4(CO)_{12}]_0 = 5.3 \times 10^{-6}, 9.7 \times 10^{-6}, 17.2 \times 10^{-6}$, and 20.7×10^{-6} mole fraction, respectively. Since very low conversions have occurred, it is convenient to consider the turnover frequency to be a constant in the vicinity of the initial reaction conditions. The turnover frequencies calculated using eqs 15 and 16, were $0.151 \pm 0.025, 0.140 \pm 0.024, 0.135 \pm 0.026$, and 0.144 ± 0.030 min^{-1}, respectively. Since the turnover frequencies have essentially the same numerical value, the reaction order a_{acyl} =

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[34] All pseudo-steady-state concentrations are reported as means and standard deviations.

[35] Precursor conversion, precursor selectivity to intermediates, and yields of intermediates have been defined previously.[12a]

[36] The exponents α_i and reaction orders a_i are reported as means and standard deviations.

$$d[C_6H_{11}CHO]/dt \equiv TOF\cdot\sum[N_i]_{ss} \qquad (15)$$

$$d[C_6H_{11}CHO]/dt \approx TOF\cdot[C_6H_{11}CORh(CO)_4]_{ss} \qquad (16)$$

1.0 in $C_6H_{11}CORh(CO)_4$ is confirmed. For the purpose of all subsequent analysis, it will be convenient to consider a power-law approximation for the turnover frequency (eq 17), where the components x_i represent the reagents C_6H_{10}, CO, and H_2.

$$TOF = k_{1obs}\prod x_i^{\alpha_i} \qquad (17)$$

Cyclohexene Concentration. The initial concentration of C_6H_{10} was systematically varied in four hydroformylation experiments performed at 293 K, 2.0 MPa of hydrogen (0.018 mole fraction), and 6.0 MPa of carbon monoxide (0.095 mole fraction). The initial concentrations of cyclohexene in mole fractions were $[C_6H_{10}]_0 = 0.054$, 0.101, 0.144, and 0.182. The corresponding initial concentrations of $Rh_4(CO)_{12}$, based on in situ IR measurements, were $[Rh_4(CO)_{12}]_0 = 1.99 \times 10^{-5}$, 1.86×10^{-5}, 1.72×10^{-5}, and 1.56×10^{-5} mole fraction.

Again, the in situ infrared spectra of the solutions, under 6.0 MPa of CO and before the addition of hydrogen, clearly showed the characteristic absorbance of the precursor $Rh_4(CO)_{12}$, the alkene C_6H_{10}, and dissolved CO, in addition to the solvent *n*-hexane. The cluster $Rh_6(CO)_{16}$ was apparently absent from solution but $Rh_2(CO)_8$ was detected.

The concentration of the intermediate $C_6H_{11}CORh(CO)_4$ as a function of time for the four experiments is shown in Figure 4. Again, after a relatively short period of 30 min, the concentrations of the intermediate $C_6H_{11}CORh(CO)_4$ became time-independent for the remaining 1000 min of each experiment. Increased $[C_6H_{10}]_0$ clearly gives rise to higher pseudo-steady-state concentrations of $C_6H_{11}CORh(CO)_4$. The maximum conversions of $Rh_4(CO)_{12}$ were $c_{max} = 11.1$, 14.0, 18.6, and 23.1% in the experiments starting with $[C_6H_{10}]_0 = 0.054$, 0.101, 0.144, and 0.182 mole fraction. The exponent in C_6H_{10} for the pseudo steady state between $Rh_4(CO)_{12}$ and $RCORh(CO)_4$ as obtained from eq 14 was $\alpha_{ene} = 0.94 \pm 0.10$.

The time-dependent concentrations of the organic product $C_6H_{11}CHO$ as a function of $[C_6H_{10}]_0$ for the four experiments are shown in Figure 5. After the induction period of approximately 30 min, the concentrations of $C_6H_{11}CHO$ are linear functions of time. Increased $[C_6H_{10}]_0$ gives rise to higher hydroformylation rates, but this effect is due to the higher yields of intermediates and not due to any intrinsic change in the velocity of the catalytic cycle. The calculated turnover frequencies were 0.138 ± 0.027, 0.147 ± 0.018, 0.135 ± 0.026, and 0.136 ± 0.027 min^{-1} at $[C_6H_{10}]_0 = 0.054$, 0.101, 0.144, and 0.182 mole fraction. The apparent reaction order is $a_{ene} = -0.02 \pm 0.05$. Therefore, cyclohexene is not involved in the rate-limiting step of the catalytic transformation of C_6H_{10} to $C_6H_{11}CHO$ under the present reaction conditions. The final conversions were 1.63, 1.42, 1.38, and 1.38%, respectively.

Carbon Monoxide Concentration. The concentration of carbon monoxide was systematically varied in four hydroformylation experiments performed at 293 K, 0.139–0.149 mole fraction of $[C_6H_{10}]_0$, and 2.0 MPa of hydrogen (0.018 mole fraction). The initial concentrations of CO in mole fractions were [CO] = 0.067, 0.082, 0.096, and 0.122 at 4.0, 5.0, 6.0, and 8.0 MPa, respectively. The corresponding initial concentrations of $Rh_4(CO)_{12}$, based on in situ IR measurements, were $[Rh_4(CO)_{12}]_0 = 1.70 \times 10^{-5}$, 1.58×10^{-5}, 1.72×10^{-5}, and 1.69×10^{-5} mole fraction. The in situ spectra were consistent with the previous kinetic experiments, and the intensity of the infrared bands corresponding to $Rh_2(CO)_8$ increased as a function of increasing CO pressure (eq 11).

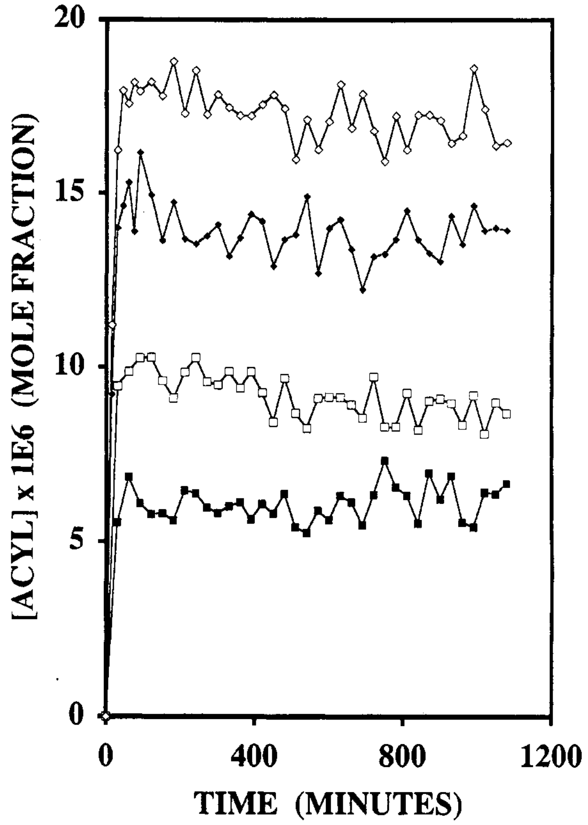

Figure 4. Effect of the initial C_6H_{10} concentration on the formation of $C_6H_{11}CORh(CO)_4$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0 = (15.6–19.9) \times 10^{-6}$ mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) $[C_6H_{10}]_0 = 0.054$, (□) $[C_6H_{10}]_0 = 0.101$, (♦) $[C_6H_{10}]_0 = 0.144$, (◊) $[C_6H_{10}]_0 = 0.182$ mole fraction.

The concentration of the intermediate $C_6H_{11}CORh(CO)_4$ as a function of time and as a function of [CO] for the four experiments is shown in Figure 6. After the first 30 min, the concentrations of the intermediate $C_6H_{11}CORh(CO)_4$ become essentially time-independent for the remaining 1000 min of each experiment. Higher liquid phase mole fractions of CO have a positive influence on the pseudo-steady-state concentration of $C_6H_{11}CORh(CO)_4$. Only 11.8, 17.1, 18.6, and 24.2% conversions of $Rh_4(CO)_{12}$ have occurred in the experiments starting with [CO] = 0.067, 0.082, 0.096, and 0.122 mole fraction. The exponent in CO obtained by regression of the pseudo-steady-state concentration data was $\alpha_{CO} = 1.089 \pm 0.097$.

The time-dependent concentrations of the organic product $C_6H_{11}CHO$, as a function of [CO] for the four experiments are shown in Figure 7. After the induction period, the concentrations of $C_6H_{11}CHO$ are linear functions of time. Changes in [CO] seem to have no net effect on the rate of formation of $C_6H_{11}CHO$, as all curves coincide. However, the calculated turnover frequencies based on $[C_6H_{11}CORh(CO)_4]$ were 0.211 ± 0.036, 0.188 ± 0.019, 0.135 ± 0.026, and 0.108 ± 0.021 min^{-1} at [CO] = 0.067, 0.082, 0.096, and 0.122 mole fraction. This leads to the apparent reaction order $a_{CO} = -1.17 \pm 0.17$. The final

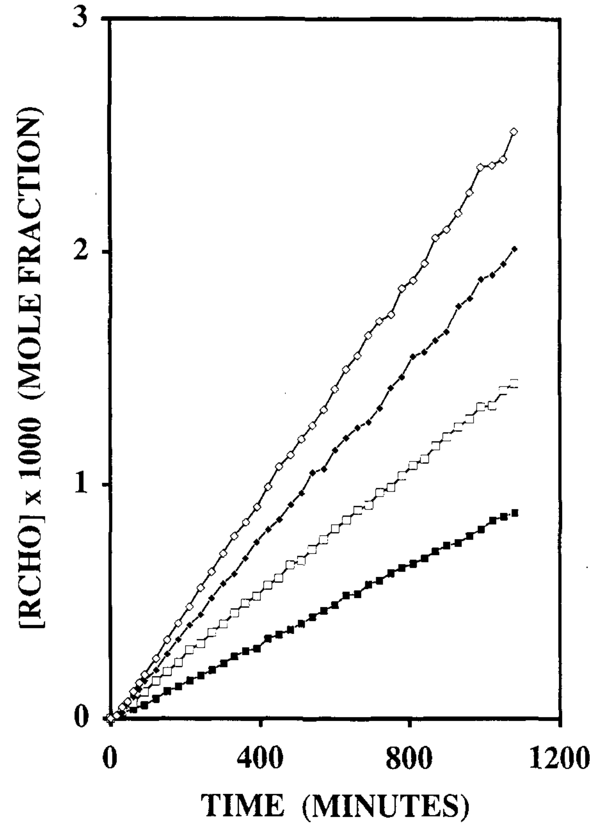

Figure 5. Effect of the initial C_6H_{10} concentration on the formation of $C_6H_{11}CHO$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0$ = (15.6–19.9) × 10^{-6} mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) $[C_6H_{10}]_0$ = 0.054, (□) $[C_6H_{10}]_0$ = 0.101, (♦) $[C_6H_{10}]_0$ = 0.144, (◇) $[C_6H_{10}]_0$ = 0.182 mole fraction.

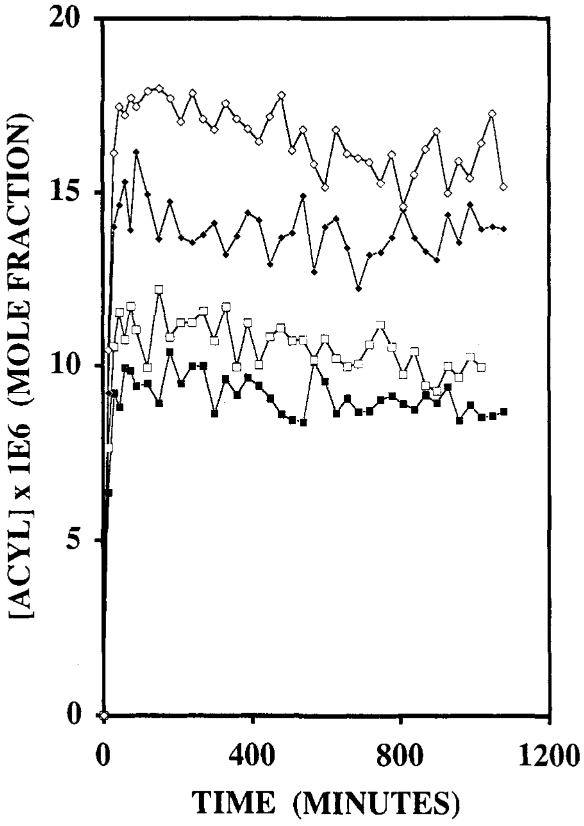

Figure 6. Effect of the carbon monoxide concentration on the formation of $C_6H_{11}CORh(CO)_4$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0$ = (15.8–17.4) × 10^{-6} mole fraction, $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) [CO] = 0.067, (□) [CO] = 0.082, (♦) [CO] = 0.096, (◇) [CO] = 0.122 mole fraction.

conversions of C_6H_{10} to $C_6H_{11}CHO$ after 18 h were 1.38, 1.35, 1.38, and 1.35% respectively.

In the above set of kinetic experiments, two state variables, namely the liquid phase mole fraction of CO and total pressure were varied simultaneously. Therefore, the exponent α_{CO} and the reaction order a_{CO} both contain a small contribution from this variation in total pressure. Though the first correction term associated with $(\partial \ln \Phi/\partial \ln x_{CO})_T$ is difficult to evaluate, the second term associated with $(\partial \ln(hk_{1obs}/kT)/\partial \ln x_{CO})_T$ is approximately $-x_jH_j(\Delta_rV^{\infty}_{x,1} + \Delta^{\ddagger}V^{\infty}_{x,1})/RT$ (see Appendix I). The numerical value of the correction term is 0.07 and the corrected reaction order is $a_{CO} = -1.10$.

Hydrogen Concentration. The concentration of dissolved hydrogen was systematically varied in four hydroformylation experiments performed at 293 K, 0.142–0.145 mole fraction of $[C_6H_{10}]_0$, and 6.0 MPa of carbon monoxide (0.095 mole fraction). The initial concentrations of hydrogen in mole fractions were $[H_2]$ = 0.009, 0.018, 0.026, and 0.034 at 1.0, 2.0, 3.0, and 4.0 MPa. The corresponding initial concentrations of $Rh_4(CO)_{12}$, based on in situ IR measurements, were $[Rh_4(CO)_{12}]_0$ = 1.59 × 10^{-5}, 1.72 × 10^{-5}, 1.55 × 10^{-5}, and 1.60 × 10^{-5} mole fraction.

The concentration of the intermediate $C_6H_{11}CORh(CO)_4$ as a function of time and as a function of the dissolved concentration of hydrogen for the four experiments is shown in Figure 8. In the experiment with only 0.009 mole fraction of hydrogen, an unusually long period of 300–400 min was required to reach the pseudo steady state. Increased liquid phase mole fractions of hydrogen clearly lead to lower pseudo-steady-state concentrations of the intermediate $C_6H_{11}CORh(CO)_4$. The exponent in H_2 for the pseudo steady state between $Rh_4(CO)_{12}$ and $RCORh(CO)_4$ and obtained by regression of the mean concentration data was $\alpha_{H_2} = -0.330 \pm 0.103$.

The time-dependent concentrations of the organic product $C_6H_{11}CHO$ as a function of $[H_2]$ for the four experiments are shown in Figure 9. After the induction periods of approximately 30–300 min, the concentrations of $C_6H_{11}CHO$ were linear functions of time. Higher liquid phase concentrations of hydrogen lead to higher rates of hydroformylation. After accounting for $[C_6H_{11}CORh(CO)_4]$ in each spectrum, the calculated turnover frequencies were 0.074 ± 0.011, 0.135 ± 0.026, 0.205 ± 0.030, and 0.292 ± 0.051 min^{-1} at $[H_2]$ = 0.009, 0.018, 0.026, and 0.034 mole fraction. The apparent reaction order in hydrogen is $a_{H_2} = 1.02 \pm 0.06$. The correction for total pressure effects gives $a_{H_2} = 1.04$ (see Appendix I). The final conversions of C_6H_{10} to $C_6H_{11}CHO$ after 18 h were 0.76, 1.38, 1.68, and 1.87%, respectively.

Effect of Temperature. The temperature of the system was systematically varied in four hydroformylation experiments performed at approximately 0.144 mole fraction of $[C_6H_{10}]_0$, 2.0 MPa of hydrogen (0.018 mole fraction), and 6.0 MPa of carbon monoxide (0.095 mole fraction). The temperatures were 283, 293, 298, and 303 K. The corresponding initial concentrations of $Rh_4(CO)_{12}$ in these experiments, based on in situ IR measurements, were $[Rh_4(CO)_{12}]_0$ = 1.40 × 10^{-5}, 1.72 × 10^{-5}, 1.49 × 10^{-5} and 1.27 × 10^{-5} mole fraction.

The concentration of the intermediate $C_6H_{11}CORh(CO)_4$ as a function of time and as a function of the system

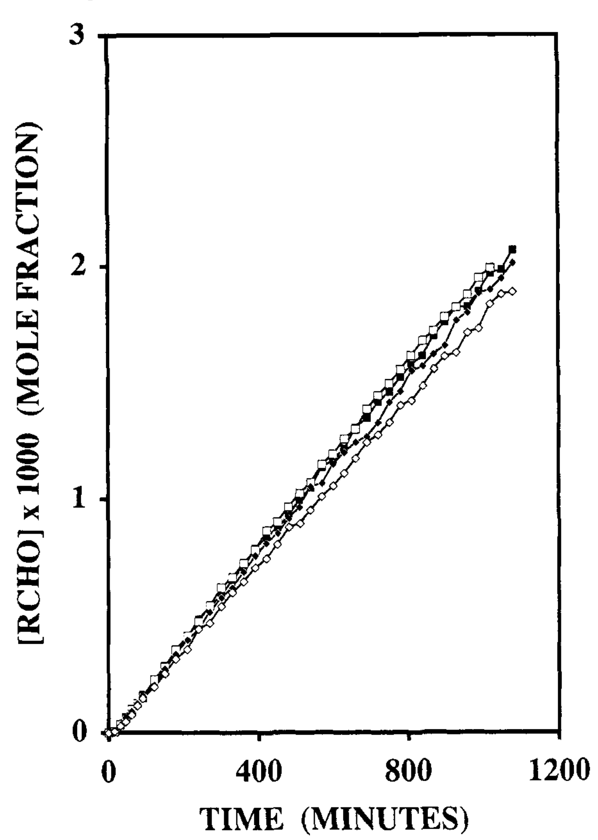

Figure 7. Effect of the carbon monoxide concentration on the formation of $C_6H_{11}CHO$ as a function of time. Conditions; $[Rh_4(CO)_{12}]_0$ = (15.8–17.4) × 10^{-6} mole fraction, $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.018 mole fraction of H_2 (2.0 MPa), in *n*-hexane at 293 K. Key: (■) [CO] = 0.067, (□) [CO] = 0.082, (♦) [CO] = 0.096, (◇) [CO] = 0.122 mole fraction.

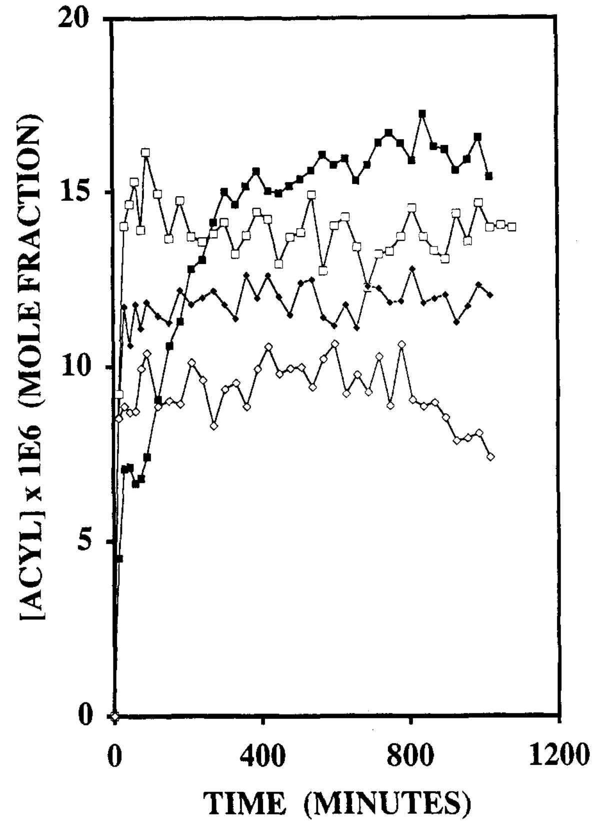

Figure 8. Effect of the hydrogen concentration on the formation of $C_6H_{11}CORh(CO)_4$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0$ = (15.5–17.2) × 10^{-6} mole fraction, $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.095 mole fraction of CO (6.0 MPa), in *n*-hexane at 293 K. Key: (■) $[H_2]$ = 0.009, (□) $[H_2]$ = 0.018, (♦) $[H_2]$ = 0.026, (◇) $[H_2]$ = 0.034 mole fraction.

temperature for the four experiments is shown in Figure 10. After the initial period of 30 min (293, 298, 303 K) or 400–500 min (283 K), the concentrations of the intermediate $C_6H_{11}CORh(CO)_4$ become time-independent for the remaining 1000 min of each experiment. Higher temperatures lead to lower conversions of $Rh_4(CO)_{12}$ to $C_6H_{11}CORh(CO)_4$. The constant Φ was 0.1214, 0.1241, 0.1031, and 0.0996 at 283, 293, 298, and 303 K, respectively. The resulting apparent enthalpy and entropy of this pseudo steady state are $\Delta_{ss}H_x = -4.7 \pm 0.3$ kJ/mol (−1.1 ± 0.1 kcal/mol) and $\Delta_{ss}S_x = -27.6 \pm 0.7$ J/(mol K) (−6.6 ± 0.2 cal/(mol K)) (see Appendix I).

The time-dependent concentrations of the organic product $C_6H_{11}CHO$, as a function of temperature for the four experiments are shown in Figure 11. After the induction period, the concentration of $C_6H_{11}CHO$ is a linear function of time. Increased system temperature leads to an increased rate of hydroformylation. The final conversions of C_6H_{10} to $C_6H_{11}CHO$ were 0.37, 1.38, 2.48, and 4.02%. The calculated turnover frequencies based on $[C_6H_{11}CORh(CO)_4]$ were 0.043 ± 0.019, 0.135 ± 0.026, 0.303 ± 0.052, and 0.514 ± 0.072 min^{-1} at T = 283, 293, 298, and 303 K. Assuming that the turnover frequency takes the limiting form TOF = $k_{1obs}[CO]^{-1}[H_2]^1[C_6H_{10}]^0$, then the activation parameters calculated using the Eyring equation are $\Delta^{\ddagger}H_x = 84.6 \pm 5.0$ kJ/mol (20.3 ± 1.2 kcal/mol) and $\Delta^{\ddagger}S_x = -8.7 \pm 17$ J/mol (−2.1 ± 4.1 cal/mol).

Other Spectroscopic Results

Reactions in Neat Cyclohexene. The hydroformylation of C_6H_{10} to $C_6H_{11}CHO$ was also carried out in neat cyclohexene at 293 K. These experiments involved the use of (a) Puriss cyclohexene after distillation from CaH_2, (b) Puriss cyclohexene after treatment with maleic anhydride to remove 1,3-cyclohexadiene and distillation from CaH_2, and (c) cyclohexene "b" with the deliberate addition of 2.5 mol % 1,3-cyclohexadiene. In contrast to dilute $C_6H_{10}/n\text{-}C_6H_{14}$ solutions, the tetranuclear rhodium complex was only sparingly soluble in neat cyclohexene.

In situ spectra taken during hydroformylation experiments using cyclohexene "a", and under the reaction conditions P_{CO} = 0.5–10.0 MPa, P_{H_2} = 0.5 MPa, and 293 K, showed incomplete precursor conversion and numerous metal carbonyl bands in addition to those arising from $Rh_4(CO)_{12}$ and $C_6H_{11}CORh(CO)_4$. The principal new absorbance maxima in the metal carbonyl region were observed at ν_{CO} = 2084, 2063, 2024, 2005, and 1986 cm^{-1}. Further, two "organic" C=O vibrations at 1732 and 1692 cm^{-1} were observed. These can be assigned to the aldehyde $C_6H_{11}CHO$ and to a ketone(s) respectively.[18e] The in situ spectra contain considerable noise, i.e., of the order of (2–3) × 10^{-2} absorbance units.

Under the reaction conditions P_{CO} = 1.0–10.0 MPa, P_{H_2} = 0.1–1.0 MPa, and 293 K, unconverted $Rh_4(CO)_{12}$ could clearly be identified in the in situ spectra taken during hydroformylations starting with cyclohexene "b". Characteristic bands for $Rh_4(CO)_{12}$ appear at 2072, 2067, 2040, and 1882 cm^{-1}. The intermediate $C_6H_{11}CORh(CO)_4$ could also be clearly identified by its absorbance maxima at 2108, 2063, 2036, 2016, and 1700 cm^{-1}. The wavenumbers for both sets of bands show strong shifts due to solvent effects. The precursor and intermediate rapidly achieve a pseudo steady state. Even in neat cyclohexene, only about 70%

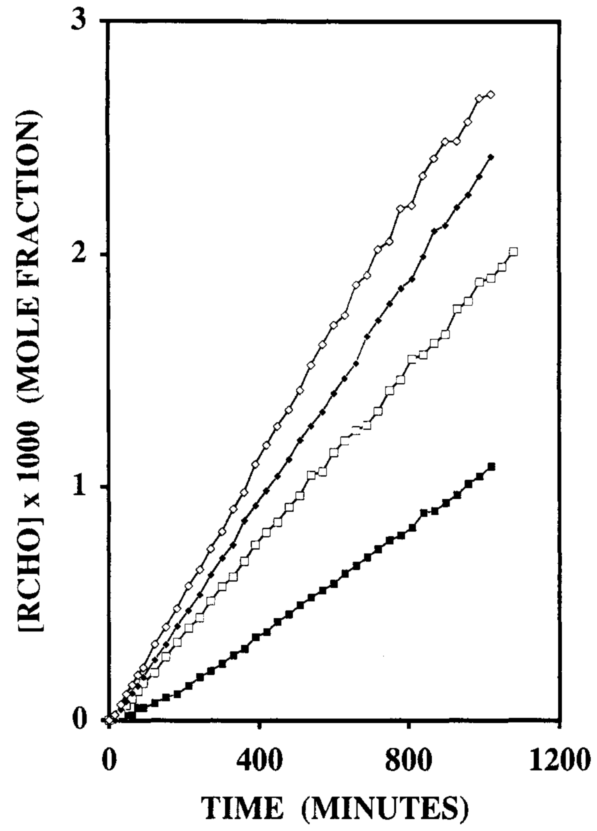

Figure 9. Effect of the hydrogen concentration on the formation of $C_6H_{11}CHO$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0$ = (15.5–17.2) × 10^{-6} mole fraction, $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.095 mole fraction of CO (6.0 MPa), in *n*-hexane at 293 K. Key: (■) $[H_2]$ = 0.009, (□) $[H_2]$ = 0.018, (♦) $[H_2]$ = 0.026, (◇) $[H_2]$ = 0.034 mole fraction.

conversion of $Rh_4(CO)_{12}$ occurs at the reaction conditions of 6.0 MPa of CO and 0.5 MPa of H_2. There is one intense band in the organic CO region, namely that at 1732 cm^{-1} for the formation of the aldehyde $C_6H_{11}CHO$.

Under the reaction conditions P_{CO} = 1.0–10.0 MPa, P_{H_2} = 0.1–1.0 MPa, and 293 K, no $Rh_4(CO)_{12}$ nor $C_6H_{11}CHORh(CO)_4$ could be identified in the in situ spectra during hydroformylations starting with cyclohexene "c". As was the case with cyclohexene "a", numerous new metal carbonyl bands arise. These new absorbance maxima occur at ν_{CO} = 2086, 2062, 2046, 2024, 2006, and 1986 cm^{-1}. The two organic C=O vibrations at 1732 and 1692 cm^{-1} belonging to $C_6H_{11}CHO$ and a ketone(s) are present. The in situ spectra contain considerable noise (Figure 12).

Discussion

Equilibrium-Controlled Precursor Conversion. After only a limited extent of precursor conversion, a pseudo steady state was established between $Rh_4(CO)_{12}$ and the intermediate $C_6H_{11}CORh(CO)_4$ in all the hydroformylation experiments. The experimentally determined expression relating the pseudo-steady-state concentrations of the two metal carbonyl complexes appears in eqs 18 and 19.

$$[C_6H_{11}CORh(CO)_4]_{ss} = \Phi[Rh_4(CO)_{12}]_{ss}^{0.3}[CO]^{1.1}[H_2]^{-0.3}[C_6H_{10}]^{0.9} \quad (18)$$

$$\Phi = \exp(4700/RT - 28/R) \quad (19)$$

The pseudo-steady-state expression for $[C_6H_{11}CORh(CO)_4]_{ss}$ arises from the equilibrium-controlled conversion of $Rh_4(CO)_{12}$. First, consider the equilibration of the precursor $Rh_4(CO)_{12}$ with the mononuclear carbonyl hydride species $\{HRh(CO)_3\}$. This equilibrium $Rh_4(CO)_{12} + 2H_2 \rightleftharpoons 4\{HRh(CO)_3\}$ can be written

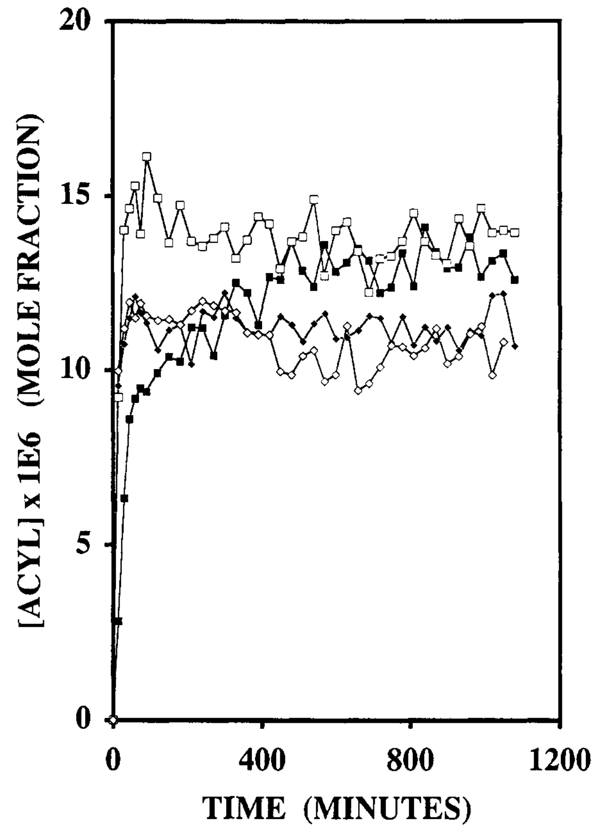

Figure 10. Effect of temperature on the formation of $C_6H_{11}CORh(CO)_4$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0$ = (12.7–17.2) × 10^{-6} mole fraction, $[C_6H_{10}]_0$ = 0.144 mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa) in *n*-hexane at 293 K. Key: (■) 283, (□) 293, (♦) 298, (◇) 303 K.

$$[HRh(CO)_3]_{eq} = (K_{eq}[Rh_4(CO)_{12}]_{eq}[H_2]^2)^{0.25} \quad (20)$$

Next, consider a pseudo-steady-state hypothesis (PSSH) for the concentration of the intermediate $\{HRh(CO)_3\}$. The rate of formation of $\{HRh(CO)_3\}$ is identically equal to the rate of hydroformylation, i.e., $k_{1obs}[C_6H_{11}CORh(CO)_4][CO]^{-1}[H_2]$ (vide infra). Further, the rate of reaction between $\{HRh(CO)_3\}$ and cyclohexene is simply $k_2[HRh(CO)_3][C_6H_{10}]$. The combined PSSH for $\{HRh(CO)_3\}$ is

$$d[HRh(CO)_3]/dt = k_{1obs}[C_6H_{11}CORh(CO)_4]_{ss}[CO]^{-1}[H_2] - k_2[HRh(CO)_3][C_6H_{10}] \quad (21)$$

$$d[HRh(CO)_3]/dt \equiv 0 \quad (22)$$

The unknown concentration of $\{HRh(CO)_3\}$ can be eliminated. This results in a relationship (eq 23) between the two observable metal carbonyls $C_6H_{11}CORh(CO)_4$ and

$$[C_6H_{11}CORh(CO)_4]_{ss} = \Phi[Rh_4(CO)_{12}]_{ss}^{0.25}[CO]^1[H_2]^{-0.5}[C_6H_{10}]^1 \quad (23)$$

$Rh_4(CO)_{12}$ where $\Phi = (K_{eq}^{0.25}k_2/k_{1obs})$. The experimentally determined exponents are in excellent agreement. With the exception of α_p, the exponents obtained from the derivation lie within ±2 standard deviations of the experimental results.

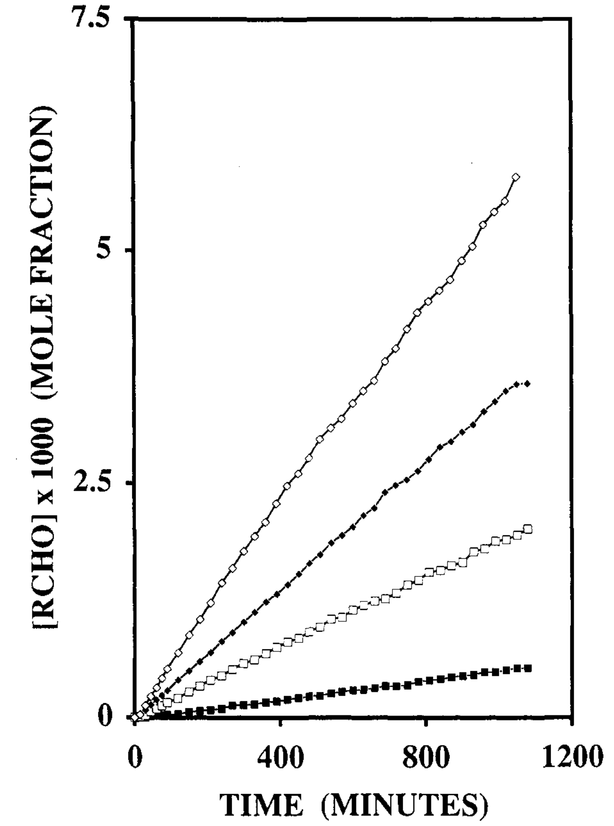

Figure 11. Effect of temperature on the formation of $C_6H_{11}CHO$ as a function of time. Conditions: $[Rh_4(CO)_{12}]_0 = (12.7–17.2) \times 10^{-6}$ mole fraction, $[C_6H_{10}]_0 = 0.144$ mole fraction, 0.095 mole fraction of CO (6.0 MPa), 0.018 mole fraction of H_2 (2.0 MPa) in *n*-hexane at 293 K. Key: (■) 283, (□), 293, (◆) 298, (◇) 303 K.

Hydrogenolysis of $C_6H_{11}CORh(CO)_4$. As shown in the series of experiments involving variations in $[Rh_4(CO)_{12}]_0$, the rate of product formation was proportional to the concentration of $[C_6H_{11}CORh(CO)_4]_{ss}$. The experimentally determined rate expression for product formation in terms of the observable $[C_6H_{11}CORh(CO)_4]_{ss}$ appears in eqs 24 and 25.

$$d[C_6H_{11}CHO]/dt = k_{1obs}[C_6H_{11}CORh(CO)_4]^1_{ss}[CO]^{-1.1}[H_2]^1[C_6H_{10}]^{0.1} \quad (24)$$

$$k_{1obs} = (kT/h)\exp(-84600/RT - 9/R) \quad (25)$$

The above rate expression indicates that the hydrogenolysis of $C_6H_{11}CORh(CO)_4$ is the rate-limiting step in the hydroformylation of cyclohexene. Specifically, the term $[CO]^{-1}[H_2]$ is consistent with (I) the existence of an equilibrium between $C_6H_{11}CORh(CO)_4$, CO and $\{C_6H_{11}CORh(CO)_3\}$ and (II) the oxidative addition of H_2 to $\{C_6H_{11}CORh(CO)_3\}$ to give the product $C_6H_{11}CHO$ and the intermediate $\{HRh(CO)_3\}$. This result supports the classic mechanistic picture of the hydroformylation reaction.[2b] In this respect the hydroformylation of cyclohexene is mechanistically similar to most other alkenes.[37]

$$C_6H_{11}CORh(CO)_4 \rightleftharpoons CO + \{C_6H_{11}CORh(CO)_3\} \quad (26)$$

$$\{C_6H_{11}CORh(CO)_3\} + H_2 \rightarrow C_6H_{11}CHO + \{HRh(CO)_3\} \quad (27)$$

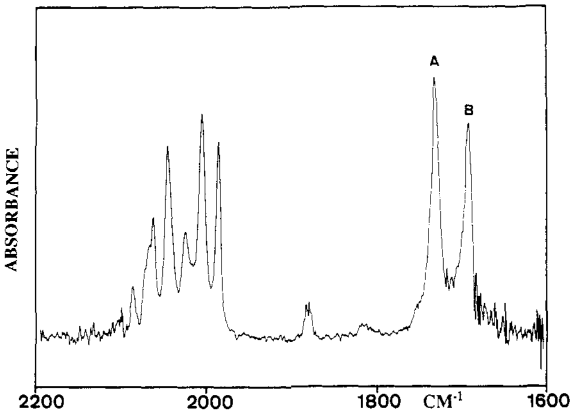

Figure 12. In situ high-pressure infrared spectrum of a hydroformylation performed in neat cyclohexene with deliberate 2.5% 1,3-cyclohexadiene impurity (cyclohexene, 1,3-cyclohexadiene, and CO subtraction). Conditions: $[Rh_4(CO)_{12}]_0 = 20 \times 10^{-5}$ mole fraction, 4.6 MPa of CO, 0.4 MPa of H_2, at 293 K. Key: (A) cyclohexanecarboxaldehyde, (B) ketone.

Overall Rates of Hydroformylation. The expressions for the pseudo steady state and the rate of product formation can be combined.[38] The resulting overall rate expression for product formation in terms of $[Rh_4(CO)_{12}]_{ss}$ is given in eq 28. In the limit of very low precursor

$$d[C_6H_{11}CHO]/dt \propto [Rh_4(CO)_{12}]^{0.25}_{ss}[CO]^0[H_2]^{0.5}[C_6H_{10}]^1 \quad (28)$$

conversion, in other words, as $[Rh_4(CO)_{12}]_{ss}$ approached $[Rh_4(CO)_{12}]_0$, eq 28 coincides with the experimental results previously obtained by Markó et al.[6]

Activation of Hydrogen. It was shown that under pseudo-steady-state conditions, the multinuclear precursor $Rh_4(CO)_{12}$ exists in equilibrium exchange with both $Rh_2(CO)_8$ and $\{HRh(CO)_3\}$. This observation suggests the continuous formation of $\{HRh(CO)_3\}$ from $Rh_2(CO)_8$ in these experiments according to the elementary steps shown in eqs 29 and 30.[39] Numerous examples of the bimolecular

$$Rh_2(CO)_8 \rightleftharpoons CO + \{Rh_2(CO)_7\} \quad (29)$$

$$\{Rh_2(CO)_7\} + H_2 \rightleftharpoons \{HRh(CO)_3\} + HRh(CO)_4 \quad (30)$$

reaction of H_2 with dinuclear metal complexes are known,[40–42] and coordinative unsaturation is a common prerequisite for such activation.

During the induction period starting with 3,3-dimethylbut-1-ene as alkene, the loss of $Rh_4(CO)_{12}$ was shown to

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(37) A low enthalpy of activation $\Delta^\ddagger H_x = 49$ kJ/mol has been measured for the hydroformylation of 3,3-dimethylbut-1-ene.[13]

(38) In power-law form, the expression $d[\text{product}]/dt = \text{TOF}\cdot\sum[N_i]_{ss}$ can be expanded as $d[C_6H_{11}CHO]/dt = k_{1obs}\prod x^{\alpha_i}\cdot f(K,k)\cdot\prod x^{\alpha_j}\cdot[\text{precursor}]^{\alpha_p}$.

(39) It has been previously suggested that the formation of $HRh(CO)_4$ may occur via the activation of molecular hydrogen on dinuclear rhodium carbonyl species. Vidal, J. L.; Schoening, R. C.; Walker, W. E. *ACS Symp. Ser.* **1980**, *155*, 61.

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be proportional to $[Rh_4(CO)_{12}][CO]^2[H_2]$.[13] Therefore, at least three modes of hydrogen activation appear to exist in alkene hydroformylations starting with $Rh_4(CO)_{12}$ as catalyst precursor. These are (I) the bimolecular reaction of H_2 with a reactive cluster $\{Rh_4(CO)_{14}\}$, (II) the reaction of H_2 with $\{Rh_2(CO)_7\}$, and (III) the hydrogenolysis of $\{RCORh(CO)_3\}$.

Binuclear Elimination. The kinetic results exclude a significant contribution to the overall hydroformylation rate from a catalytic binuclear elimination reaction,[43,44] at least under the present reaction conditions and at the very low nominal metal loadings used in these experiments. Indeed, for the experiments performed with variations in $[Rh_4(CO)_{12}]_0$ and hence variations in $[C_6H_{11}CORh(CO)_4]_{ss}$, the calculated turnover frequencies were the same. The rate of hydroformylation is simply a linear function of $[C_6H_{11}CORh(CO)_4]_{ss}$, there are no higher order terms. These results do not exclude the existence per se of a binuclear elimination reaction between mononuclear rhodium species (eq 31). Such a mechanism is analogous to the stoichiometric Heck–Breslow reaction between acyl cobalt carbonyls and cobalt carbonyl hydrides.[45]

$$RCORh(CO)_x + HRh(CO)_y \rightarrow RCHO + Rh_2(CO)_{x+y} \quad (31)$$

Neat Cyclohexene and the Presence of 1,3-Cyclohexadiene. Neat cyclohexene, free from the impurity 1,3-cyclohexadiene, was not chosen for use in the kinetic studies since (I) the precursor $Rh_4(CO)_{12}$ was only sparingly soluble, (II) solubility data for CO and H_2 in cyclohexene are not available and (III) an exceptionally low signal to noise level was obtained in the resulting difference spectra. The latter probably indicates the formation of other rhodium complexes in solution, at concentrations sufficiently high as to adversely affect the quality of the in situ spectra.

Concerning impurities, it seems reasonable that allylrhodium carbonyl complexes and possibly alkylrhodium carbonyl complexes are formed in observable quantities in the experiments containing trace 1,3-cyclohexadiene. This would explain both the new ν_{CO} absorbance as well as the ketone group at 1692 cm^{-1}. Indeed, the reaction of conjugated dienes with acylcobalt carbonyls, leading to insertion into the acyl–cobalt bond and to the generation of allyl intermediates has been conclusively shown.[46] Accordingly, a plausible reaction scheme for the formation of free ketone is presented in eqs 32–35. The formation of ketones starting with conjugated dienes under hydroformylation conditions has been noted in the literature.[47]

$$C_6H_{10} + HRh(CO)_3 + CO \rightarrow \rightarrow C_6H_{11}CORh(CO)_3 \quad (32)$$

$$C_6H_{11}CORh(CO)_3 + C_6H_8 \rightarrow C_6H_{11}CORh(CO)_3(C_6H_8) \quad (33)$$

$$C_6H_{11}CORh(CO)_3(C_6H_8) \rightarrow C_6H_{11}COC_6H_8Rh(CO)_3 \quad (34)$$

$$C_6H_{11}COC_6H_8Rh(CO)_3 + H_2 \rightarrow C_6H_{11}COC_6H_9 + HRh(CO)_3 \quad (35)$$

Conclusions

There appear to be two primary reasons for the problems previously encountered during kinetic studies of the hydroformylation of cyclohexene starting with unmodified rhodium complexes. The first involves the presence of 1,3-cyclohexadiene as a common, almost omnipresent, impurity in cyclohexene. The presence of trace quantities of 1,3-cyclohexadiene gives rise to significant quantities of other rhodium complexes. These complexes most likely include, but are not restricted to, allylrhodium intermediates.

Secondly, the overall rates of cyclohexene hydroformylation are difficult to interpret, even in the absence of 1,3-cyclohexadiene, due to equilibrium-controlled conversion of $Rh_4(CO)_{12}$. This phenomenon of equilibrium-controlled precursor conversion gives rise to very complex overall kinetic expressions for product formation at the pseudo steady state. In the present study, the use of in situ spectroscopic measurements has allowed the separation of the overall and observable hydroformylation rate into terms representing the equilibrium-controlled conversion of precursor and the turnover frequency.

Acknowledgment. This work was supported by the "Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung". We thank the University of Lund for a scholarship for C.F. Discussions with Professor L. M. Venanzi and Professor D. W. T. Rippin are greatly appreciated.

Appendix I

Pressure and Temperature Dependencies. A chemical equilibrium constant $K_{eq}(P_T,T)$ can be written in expanded form in terms of a standard enthalpy of reaction $\Delta_r H°$ evaluated at some reference pressure P_0, the standard entropy of reaction $\Delta_r S°$, and the volume of reaction $\Delta_r V^\infty$ at infinite dilution.[48] It is implicit that the present standard state consists of the reactants (solutes) at infinite dilution in *n*-hexane and at some reference pressure, i.e.,

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[43] (a) The stoichiometric binuclear elimination reaction between two mononuclear organometallic complexes can be written $RML_m + R^*M^*L_n \rightarrow RR^* + MM^*L_{m+n}$. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

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[47] (a) Adkins, H.; Williams, J. L. R. *J. Org. Chem.* **1952**, *17*, 980. (b) Dokiya, M.; Bando, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1741.

[48] Guggenheim, E. A. *Trans. Faraday Soc.* **1936**, *33*, 607.

P_0 = 0.1 MPa.

$$K_{eq}(P_T,T) = \exp[(-\Delta_r H^\circ(P_0) + \Delta_r S^\circ T - \Delta_r V^\infty(P_T - P_0))/RT] \quad (A1)$$

From transition state theory, rate constants $k_i(P_T,T)$ can be written in terms of the Planck constant h, the Boltzmann constant k, and an expansion containing the standard enthalpy of activation $\Delta^\ddagger H^\circ$, the standard entropy of activation $\Delta^\ddagger S^\circ$, and the volume of activation $\Delta^\ddagger V^\infty$ (Eyring equation).[49] Again, the standard state consists of the reactants (solutes) at infinite dilution in n-hexane and at some reference pressure, i.e., P_0 = 0.1 MPa.

$$k_i(P_T,T) = (kT/h)\exp[(-\Delta^\ddagger H^\circ(P_0) + \Delta^\ddagger S^\circ T - \Delta^\ddagger V^\infty(P_T - P_0))/RT] \quad (A2)$$

The hydrogenolysis of the intermediate $C_6H_{11}CORh(CO)_4$ is a nonelementary transformation consisting of a preequilibrium involving $\{C_6H_{11}CORh(CO)_3\}$ followed by the oxidative addition of hydrogen. Therefore, the observed rate constant k_{1obs} is actually the product of an equilibrium constant K_1 and a rate constant k_1

$$k_{1obs} = K_1 k_1 \quad (A3)$$

Let x_j represent the liquid phase concentration of either carbon monoxide or hydrogen. Then, the partial derivative $(\partial \ln(hk_{1obs}/kT)/\partial \ln x_j)_T$ represents the difference between the apparent and real reaction orders (eqs A4 and A5). It is convenient to evaluate both H_j and x_j at the mean experimental value $\bar{x}_j$.

$$a_{j,app} = a_j + (\partial \ln(hk_{1obs}/kT)/\partial \ln x_j)_T \quad (A4)$$

$$(\partial \ln(hk_{1obs}/kT)/\partial \ln x_j)_T \approx -x_j H_j(\Delta_r V^\infty{}_{x,1} + \Delta^\ddagger V^\infty{}_{x,1})/RT \quad (A5)$$

The volume of reaction $\Delta_r V^\infty{}_{x,1}$ is positive, and a realistic upper bound is obtained from the partial molar volume of carbon monoxide, i.e, v_{CO} = 52 mL/mol. Indeed, studies of the equilibrium $CoRh(CO)_8 \rightleftharpoons CO + CoRh(CO)_7$ have given a value of $\Delta_r V^\infty{}_x$ = 45 mL/mol.[50] Further, the activation volume for the oxidative addition of molecular hydrogen to a single metal center, i.e., *trans*-$IrCl(CO)(PPh_3)_2$, has been determined as $\Delta^\ddagger V^\infty{}_{x,1}$ = −20 mL/mol.[51] These observations suggest that the apparent activation volume $\Delta^\ddagger V^\infty{}_{x,1obs} = (\Delta_r V^\infty{}_{x,1} + \Delta^\ddagger V^\infty{}_{x,1})$ may be on the order of 25 mL/mol.

In an analogous manner, the term $\Phi = (K_{eq}^{0.25} k_2/k_{1obs})$ for the pseudo-steady-state concentration of $C_6H_{11}CORh(CO)_4$ can be analyzed. The expression $RT^2(\partial \ln \Phi/\partial T)_P$ defines the apparent enthalpy $\Delta_{ss}H_x$ of the pseudo steady state (eq A6) and provides a relationship for the apparent enthalpy as a combination of enthalpies of reaction and enthalpies of activation (eq A7).

$$RT^2(\partial \ln \Phi/\partial T)_P \equiv \Delta_{ss}H_x \quad (A6)$$

$$\Delta_{ss}H_x = 0.25\cdot\Delta_r H_{x,eq} - \Delta_r H_{x,1} - \Delta^\ddagger H_{x,1} + \Delta^\ddagger H_{x,2} \quad (A7)$$

The expression $(\partial RT \ln \Phi/\partial T)_P$ defines the apparent entropy $\Delta_{ss}S_x$ of the pseudo steady state (eq A8) and provides a relationship for the apparent entropy as a combination of equilibrium and activation parameters (eq A9).

$$(\partial RT \ln \Phi/\partial T)_P \equiv \Delta_{ss}S_x \quad (A8)$$

$$\Delta_{ss}S_x = 0.25\cdot\Delta_r S_{x,eq} - \Delta_r S_{x,1} - \Delta^\ddagger S_{x,1} + \Delta^\ddagger S_{x,2} \quad (A9)$$

Again, let x_j represent the liquid phase concentration of either carbon monoxide or hydrogen. Then, evaluation of the partial derivative $(\partial \ln \Phi/\partial \ln x_j)_T$, leads to an expression relating the apparent and real exponents α_j (eqs A10 and A11). Unfortunately, no reliable experimental data presently exist in order to evaluate the magnitude of $\Delta_r V^\infty{}_{x,eq}$, and $\Delta^\ddagger V^\infty{}_{x,2}$.

$$\alpha_{j,app} = \alpha_j + (\partial \ln \Phi/\partial \ln x_j)_T \quad (A10)$$

$$(\partial \ln \Phi/\partial \ln x_j)_T \approx -x_j H_j[0.25\cdot\Delta_r V^\infty{}_{x,eq} - \Delta_r V^\infty{}_{x,1} - \Delta^\ddagger V^\infty{}_{x,1} + \Delta^\ddagger V^\infty{}_{x,2}]/RT \quad (A11)$$

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