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The Unmodified Homogeneous Rhodium-Catalyzed Hydroformylation of Cyclohexene and the Search for Monometallic Catalytic Binuclear Elimination

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The homogeneous catalytic hydroformylation of cyclohexene to cyclohexanecarboxaldehyde was studied, starting with $Rh_4(CO)_{12}$ as catalyst precursor in *n*-hexane as solvent. The reaction conditions were $T = 298$ K, $P_{H_2} = 2.0$ MPa (0.018 mol fraction), $P_{CO} = 6.0$ MPa (0.095 mol fraction), and $[C_6H_{10}]_0 = 0.144$ mol fraction. The nominal rhodium concentration was varied in four experiments as $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$, 6.6×10^{-5}, 1.7×10^{-4}, and 3.3×10^{-4} mol fraction (where the last value represents the approximate solubility limit). In each of the four experiments the time-dependent concentrations of the precursor $Rh_4(CO)_{12}$, the organometallic 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. Complete conversion of the precursor $Rh_4(CO)_{12}$ to the intermediate $C_6H_{11}CORh(CO)_4$ was never observed during the 8 h experiments. Instead, after approximately 30 min, a pseudo steady state was achieved between the species $Rh_4(CO)_{12}$ and $C_6H_{11}CORh(CO)_4$. The hydrogenolysis of $C_6H_{11}CORh(CO)_4$ resulted in aldehyde formation, and only 1.04−1.94% conversion of C_6H_{10} was observed in any 8 h experiment. The turnover frequencies (TOF), based on the instantaneous concentrations of $C_6H_{11}CORh(CO)_4$, were calculated at 15 min intervals for all four experiments, and the data were regressed according to the polynomial $TOF = (k_1 + k_2K_{eq}[Rh_4(CO)_{12}]^{0.25})$. The evaluated coefficients were $k_1 = (2.11 \pm 0.06) \times 10^{-3}\ s^{-1}$ and $k_2K_{eq} = (0.50 \pm 0.60) \times 10^{-3}\ s^{-1}$, where the term $k_2K_{eq}\ [Rh_4(CO)_{12}]^{0.25}$ is ca. $5 \times 10^{-5}\ s^{-1}$. These results strongly suggest that there is no statistically significant contribution to aldehyde formation from a monometallic catalytic binuclear elimination in the rhodium-catalyzed hydroformylation reaction under these conditions.

Introduction

During early investigations of the mechanism of the hydroformylation reaction, Heck and Breslow showed that a stoichiometric binuclear elimination reaction exists between pre-prepared solutions of $HCo(CO)_4$ and $CH_3COCo(CO)_3$, resulting in aldehyde formation (eq 1) and the dinuclear complex $Co_2(CO)_8$.[1] In this landmark

$$HCo(CO)_4 + CH_3COCo(CO)_4 \rightarrow CH_3CHO + Co_2(CO)_8 \quad (1)$$

study, the reactions were run in the absence of dissolved hydrogen and dissolved carbon monoxide—i.e., under conditions far removed from the catalytic case. Subsequently, numerous studies have shown that *stoichiometric* binuclear elimination reactions are possible between $HCo(CO)_4$ and a variety of substituted cobalt tetracarbonyls $RCo(CO)_4$.[2]

Although the existence of binuclear elimination reactions associated with the hydroformylation reaction has been clearly demonstrated in the stoichiometric case, solid experimental evidence for the existence of catalytic binuclear elimination under catalytic conditions has been difficult to obtain. Whyman, Alemdaroglu et al., and Mirbach have all undertaken spectroscopic studies of the cobalt-catalyzed hydroformylation reaction.[3−5] In these experiments, the simultaneous presence of both $HCo(CO)_4$ and $RCOCo(CO)_4$ (R = octyl, cyclohexyl) was observed during the catalytic hydroformylations. Regression of the kinetic data by Mirbach indicated that perhaps 3% of all product formation occurs via a catalytic binuclear elimination reaction (CBER). However, the statics associated with the regressed coefficients were unfortunately not presented.

Over the past decade, numerous detailed in situ spectroscopic and kinetic studies of the unmodified rhodium-catalyzed hydroformylation have been made.[6−11]

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(1) (a) Breslow, D. S.; Heck, R. F. *Chem. Ind. (London)* **1960**, 467. (b) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 4023. (c) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974.

(2) (a) Ungvary, F.; Marko, L. *Organometallics* **1982**, *1*, 1120. (b) Azran, J.; Orchin, M. *Organometallics* **1984**, *3*, 197. (c) Kovacs, I.; Ungvary, F.; Marko, L. *Organometallics* **1986**, *5*, 209.

(3) (a) Whyman, R. *J. Organomet. Chem.* **1974**, *81*, 97. (b) Whyman, R. *J. Organomet. Chem.* **1974**, *66*, C23.

(4) Mirbach, M. F. *J. Organomet. Chem.* **1984**, *265*, 205.

(5) (a) van Hoven, M.; Alemdaroglu, N. H.; Penninger, J. M. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1975**, *14*, 259. (b) Alemdaroglu, N. H.; Penninger, J. M. L.; Oltay, E. *Monatsh. Chem.* **1976**, 1043.

(6) Garland, M.; Bor, G. *Inorg. Chem.* **1989**, *28*, 410.

(7) Garland, M.; Pino, P. *Organometallics* **1991**, *10*, 1693.

(8) Garland, M. *Organometallics* **1993**, *12*, 535.

(9) Fyhr, C.; Garland, M. *Organometallics* **1993**, *12*, 1753.

(10) Volker, R.; Garland, M. Manuscript in preparation.

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In these studies, the cluster fragmentation of $Rh_4(CO)_{12}$ was always observed, the formation of the mononuclear acyl complex $RCORh(CO)_4$ (R = alkyl) always occurred, and the rate of aldehyde formation was always proportional to the instantaneous concentration of the acyl species. In most of these studies, it was possible to measure the organometallic concentrations with a sensitivity of approximately 1 ppm. Despite this sensitivity, the presence of $HRh(CO)_4$ was never observed under catalytic conditions, although its existence under very severe noncatalytic conditions has been reported.[12] Thus, in contrast to the case of cobalt-catalyzed hydroformylation where both the hydride and acyl complexes are simultaneously observable, the case of rhodium-catalyzed hydroformylation only results in the observation of the acyl intermediate.

In the unusual case of cyclohexene hydroformylation, a pseudo steady state between the liquid-phase concentrations of $Rh_4(CO)_{12}$ and $C_6H_{11}CORh(CO)_4$ occurred—i.e., there was equilibrium-controlled precursor conversion.[9] Due to the experimentally determined functional form for the interdependence of the concentrations, it was concluded that hydrido rhodium carbonyls $HRh(CO)_z$ must exist in equilibrium with the cluster precursor $Rh_4(CO)_{12}$:[9]

$$Rh_4(CO)_{12} + 2H_2 + xCO \rightleftarrows 4HRh(CO)_{3+x/4} \quad (2)$$

In the present contribution, we re-examine the kinetics of the homogeneous rhodium-catalyzed hydroformylation of cyclohexene with the explicit purpose of quantifying any possible contribution of a CBER to product formation. In contrast to the previous study, which was made with ppm metal loadings,[9] much higher nominal rhodium concentrations are used in these experiments. Indeed, the concentrations of the sparingly soluble cluster $Rh_4(CO)_{12}$ are extended to their solubility limit (ca. 2000 mg/L of *n*-hexane). If aldehyde formation occurs due to both the classic unicyclic mechanism as well as a CBER, then the rate of product formation should take the general form given by eq 3.

$$\text{rate} = (k_1 + k_2K_{eq}[Rh_4(CO)_{12}]^{0.25})[RCORh(CO)_4] \quad (3)$$

In the following, four detailed kinetic experiments are performed. The rate of product formation is regressed according to eq 3, and the statistical evidence for a monometallic CBER is examined.

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.95%, Saxol, Singapore) or argon (99.95%, Saxol, Singapore) atmosphere using standard Schlenk techniques.[13] Both gases were passed through deoxy and zeolite columns before use. $Rh_4(CO)_{12}$ was purchased from Strem Chemicals (Newport, MA) and was used as obtained. Puriss quality *n*-hexane (Fluka AG, Buchs, Switzerland) was refluxed from sodium−potassium alloy under argon. Puriss quality cyclohexanecarboxaldehyde (99%, Merck, Darmstadt, Germany) was used as obtained for calibrations. Reactions were carried out under carbon monoxide (99.97%, British Oxygen Co., U.K.) and hydrogen (99.999%, Saxol, Singapore) after further purification through deoxy and zeolite columns.

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 analysis using a 10 m capillary column containing a Series 5, 30 μm fused silica column (HP, Singapore). The cyclohexene was refluxed with 2 equiv of maleic anhydride until no further 1,3-cyclohexadiene could be detected by GC.[14] The resulting cyclohexene was repeatedly washed with distilled water, passed over 4-A molecular sieves, distilled from CaH_2, and stored under argon at 273 K. As noted elsewhere, trace impurities of 1,3-cyclohexadiene are known to lead to irreproducible and/or intractable kinetic results.[9]

Equipment. Kinetic studies were performed in a 1.5 L stainless steel (SS316) autoclave (Büchi-Uster, 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-presssure membrane pump (Model DMK 30, Orlita AG, Geissen, Germany) with a maximum rating of 32.5 MPa and a 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 Polyscience Model 9505 cryostat and could be maintained isothermal ($\Delta T \leq 0.5$ °C) at 25 °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 1.0, 5.0, 10.0 piezocrystals were used for pressure measurements (Keller AG, Winterthur, Switzerland). All gases used in the kinetic experiments were purified through deoxy and zeolite columns. The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Zürich of SS316 steel and could be heated and 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 Teflon spacers were used between the windows. The construction of the flow-through cell[15] is a variation on a design due to Noack[16] and differs in some respects from other high-pressure infrared cells described in the literature (for a review, see Whyman[17]). The high-pressure cell was situated in a Perkin-Elmer System 2000 Fourier transform infrared spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A schematic diagram of the experimental setup has been given previously.[11]

Spectroscopic Aspects. Four normal infrared cells with CaF_2 windows were assembled for calibration. The optical path lengths were measured using the interference equations for parallel plates.[18] The measured optical path lengths were 0.05. 0.215, 0.525, and 1.0 mm.

The infrared absorbance spectra of the solvent *n*-hexane,[19] the reagent C_6H_{10},[20] and the product $C_6H_{11}CHO$,[21] are all well-

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[11] Feng, J.; Garland M. *Organometallics* **1999**, *18*, 417.

[12] Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249.

[13] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986.

[14] The Diels−Alder reaction between 1,3-cyclohexadiene and maleic anhydride is quantitative, yielding *endo*-bicyclo[2.2.2]-5-octene-1,2-dicarboxylic anhydride. (b) Kloetzel, M. C. *Org. React.* **1948**, *4*, 1. (b) Grieger, R. A.; Eckert, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 7149.

[15] Dietler, U. K. Dissertation, ETH-Zurich, 1974; No. 5428.

[16] Noack, K. *Spectrochim. Acta* **1968**, *24A*, 1917.

[17] Whyman, R. In *Laboratory Methods in Vibrational Spectroscopy*, 3rd ed.; Willis, H. A., van der Maas, J. H., Miller, R. G. J., Eds.; Wiley: New York, 1987; Chapter 12.

[18] Born, M.; Wolf, E. *Principles of Optics*; Pergamon: Oxford, U.K., 1975; p 360.

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documented. Both *n*-hexane and C_6H_{10} have absorbance minima at 1234 and 1257 cm^{-1} and an absorbance maximum at 1247.5 cm^{-1}. A solution consisting of 30 mL of C_6H_{10} dissolved in 200 mL of *n*-hexane was prepared, and the absorbance of the mixture was measured in the four standard cells. The absorptivity for the mixture $\epsilon_{1247.5} = 0.911 \pm 0.002$ L/(mol cm), was determined using the standard Lambert−Beer law, where *c* is concentration in mol/L and *d* is the optical path length in cm:

$$A_i = \epsilon_i c_i d \tag{4}$$

The organic product $C_6H_{11}CHO$ has a prominent absorbance maximum at 1734 cm^{-1} due to the C=O stretching mode.[22] The absorptivity of $C_6H_{11}CHO$ was taken as $\epsilon_{1734} = 372$ L/(mol cm).[9]

The tetranuclear carbonyl $Rh_4(CO)_{12}$ has absorbance maxima at 2074, 2068, 2061, 2043, and 1885 cm^{-1} in *n*-hexane.[23] The prominent band at 1885 cm^{-1} is due to the stretching mode of the bridged carbonyl ligands. The absorptivity was determined in the high-pressure cell from absorbance data obtained at the beginning of the four kinetic experiments after solvent subtraction. The experimentally determined absorptivity for $Rh_4(CO)_{12}$ in a solution of C_6H_{10}/*n*-hexane/CO was $\epsilon_{1885} = 6691 \pm 181$ L/(mol cm).

The acyl intermediate $C_6H_{11}CORh(CO)_4$ has absorbance maxima at 2111, 2065, 2039, 2020, and 1698 cm^{-1}, consistent with initial studies of the spectra and symmetry of these types of complexes.[6] The absorptivity was determined in the high-pressure cell from data obtained from the four kinetic experiments. Thirty-two spectra were recorded during each kinetic run. The absorbances from the solvent and $Rh_4(CO)_{12}$ were subtracted from each spectrum prior to the estimation of the absorbance due to $C_6H_{11}CORh(CO)_4$. The data were analyzed by taking into consideration the mass balance for rhodium (eq 5), where *N* is the amount in moles. The experimentally

$$N^{acyl} = 4N_0^{Rh_4} - 4N_t^{Rh_4} \tag{5}$$

determined absorptivity of $C_6H_{11}CORh(CO)_4$ in the reaction solution consisting primarily of C_6H_{10}/*n*-hexane/CO/H_2 was $\epsilon_{2020} = 2493 \pm 145$ L/(mol cm).

The mole fractions of the species $Rh_4(CO)_{12}$, $C_6H_{11}CORh(CO)_4$, and $C_6H_{11}CHO$ were calculated during the hydroformylation experiments from in situ absorbance measurements, using the dimensionless Lambert−Beer law (eq 6).[24] The term

$$x_i = x_{C_6}(A_i \epsilon_{1247.5})/(A_{1237.5}\epsilon_i) \tag{6}$$

x_{C_6} is the sum total of the mole fractions of both hydrocarbons, namely *n*-hexane and cyclohexene, under the initial reaction conditions.

High-resolution in situ IR spectroscopic measurements of the unmodified rhodium-catalyzed hydroformylation of cyclohexene, including the intermediate $C_6H_{11}CORh(CO)_4$, have appeared elsewhere and will not be repeated here.[9]

Kinetic Studies. Four kinetic experiments were performed. These experiments differed due to the nominal loading of rhodium in each.

Each experiment was performed in a similar manner. First, single-beam background spectra of the IR sample chamber were recorded. Then, 30 mL of cyclohexene was dissolved in 150 mL of *n*-hexane and this solution was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, infrared spectra of the C_6H_{10} solution in the high-pressure cell were recorded. The total system pressure was raised to 6.0 MPa of CO, and the stirrer and high-pressure membrane pump were started. After equilibration, infrared spectra of the C_6H_{10}/*n*-hexane/CO solution in the high-pressure cell were recorded. A solution of $Rh_4(CO)_{12}$ dissolved/suspended in 50 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurized with CO, and then added to the autoclave. Infrared spectra of the C_6H_{10}/*n*-hexane/CO/$Rh_4(CO)_{12}$ solution in the high-pressure cell were recorded. The hydroformylation kinetic runs were started by adding 2.0 MPa of hydrogen. Spectra were recorded at 15 min intervals over the interval 1100−2500 cm^{-1}. A considerable number of spectral subtractions were performed on each reaction spectrum in order to obtain the absorbance of $Rh_4(CO)_{12}$, $C_6H_{11}CORh(CO)_4$, and $C_6H_{11}CHO$ and then their instantaneous mole fraction concentrations according to eq 6.

The solubility of CO under these reaction conditions was approximately 0.095 mole fraction, and the solubility of H_2 was approximately 0.018 mole fraction.[9] Consequently, the moles in each experiment were 1.51 mol of *n*-hexane, 0.29 mol of C_6H_{10}, 0.17 mol of CO, and 0.03 mol of H_2. The amounts of $Rh_4(CO)_{12}$ used in the four experiments were 50.0, 99.5, 249.2, and 501.4 mg. The corresponding in situ measured *initial* concentrations of $Rh_4(CO)_{12}$ in the four kinetic experiments were 3.5×10^{-5}, 6.6×10^{-5}, 1.7×10^{-4}, and 3.3×10^{-4} mol fraction.

The present hydroformylation reactions were performed under negligible gas−liquid mass transfer resistance. The experimentally measured overall mass transfer coefficients $K_L a$ for hydrogen and carbon monoxide into *n*-hexane at 200 rpm was approximately 0.1 and 0.6 s^{-1}, respectively, as determined using the method of Deimling.[25] Since the maximium observed rate of hydroformylation in this study was 2×10^{-7} mol s^{-1}, all experiments belong to the category of infinitely slow reaction with respect to gas−liquid mass transfer (i.e. the kinetic regime, Hatta category H).[26] 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.[27]

In any single 8 h kinetic experiment, less than 0.006 mol conversion (1.94%) of C_6H_{10} to $C_6H_{11}CHO$ occurred. Therefore, the partial pressures of hydrogen and carbon monoxide in the closed-batch autoclave changed less than 1% during each 8 h experiment. This partial pressure change was considered to be negligible and, hence, the 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 C_6H_{10} to $C_6H_{11}CHO$, were calculated from the concentrations using a central difference approximation. The central difference approximation was chosen, since it provides an accurate approximation of the derivative from sets of smooth monotoni-

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(19) (a) Pounchert, C. L. *The Aldrich Library of Infrared Spectra*; Aldrich: Milwaukee, WI, 1981; p 3. (b) *The Sprouse Collection of Infrared Spectra*; Hansen, D., Ed.; Sprouse Sc.: Paoli, PA, 1990; Vol. 4, p 2.

(20) (a) Pounchert, C. L. *The Aldrich Library of Infrared Spectra*; Aldrich: Milwaukee, WI, 1981; p 30. (b) *The Sprouse Collection of Infrared Spectra*; Hansen, D., Ed.; Sprouse Sc.: Paoli, PA, 1990; Vol. 4, p 40.

(21) Pounchert, C. L. *The Aldrich Library of Infrared Spectra*; Aldrich: Milwaukee, WI, 1981; p 280.

(22) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds,* 4th ed.; Wiley: New York, 1991; p 119.

(23) (a) Beck, W,; Lottes, K. *Chem. Ber.* **1961**, *94*, 2378. (b) Bor. G.; Sbrignadello, G.; Noack, K. *Helv. Chim. Acta* **1975**, *58*, 815.

(24) McClure, G. L. In *Laboratory Methods in Vibrational Spectroscopy*, 3rd ed.; Willis, H. A., van der Maas, J. H., Miller, R. G. J., Eds.; Wiley: New York, 1987; Chapter 7.

(25) Deimling, A.; Karandikar, B. M.; Shah, Y. T.; Carr, N. L. *Chem. Eng. J.* **1984**, *29*, 127.

(26) Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1972; p 418.

(27) Bhattacharya, A.; Chaudari, R. V. *Ind. Eng. Chem. Res.* **1987**, *26*, 1168.

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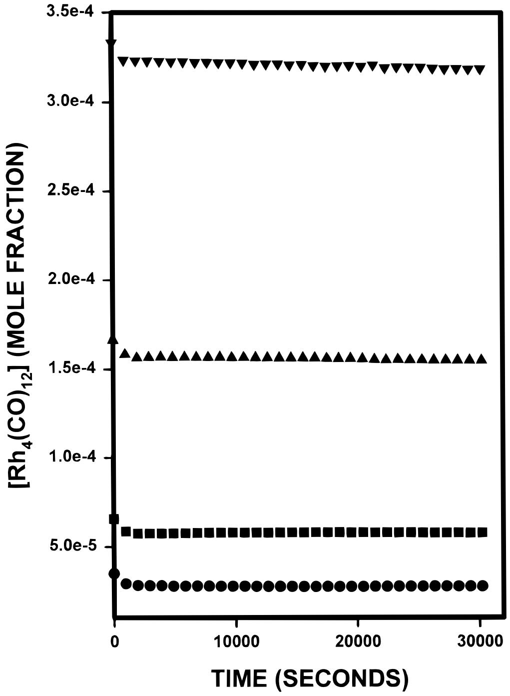

Figure 1. Time-dependent mole fraction concentrations of the precursor $Rh_4(CO)_{12}$ in the four kinetic experiments. $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$ (●), 6.6×10^{-5} (■), 1.7×10^{-4} (▲), and 3.3×10^{-4} mol fraction (▼).

cally increasing or decreasing experimental data.[28] In addition, extensive investigations concerning the numerical evaluation of turnover frequencies in homogeneous catalytic systems support the central difference approximation.[29]

Results and Discussion

Time-Dependent Concentrations. The time-dependent concentrations of the catalyst precursor $Rh_4(CO)_{12}$ are shown in Figure 1. After approximately 30 min, the pseudo steady state concentrations of $Rh_4(CO)_{12}$ were obtained. The concentrations were $[Rh_4(CO)_{12}]_{SS} = (2.71 \pm 0.01) \times 10^{-5}$, $(5.79 \pm 0.01) \times 10^{-5}$, $(15.60 \pm 0.06) \times 10^{-5}$, and $(32.09 \pm 0.12) \times 10^{-5}$ mol fraction in the experiments with $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$, 6.6×10^{-5}, 1.7×10^{-4}, and 3.3×10^{-4} mol fraction. Accordingly, only 20.7%, 11.9%, 6.2%, and 3.7% of conversion occurred during the 8 h hydroformylation experiments.

The time-dependent concentrations of the acyl intermediate, namely $C_6H_{11}CORh(CO)_4$, show a similar behavior. The intermediate rapidly forms in the first 30 min of reaction, after which a pseudo steady state is achieved (Figure 2). Regressions of the pseudo steady state concentrations provide the numerical values $[C_6H_{11}CORh(CO)_4]_{SS} = (2.63 \pm 0.04) \times 10^{-5}$, $(2.95 \pm 0.02) \times 10^{-5}$, $(3.72 \pm 0.05) \times 10^{-5}$, and $(4.37 \pm 0.03) \times 10^{-5}$ mol fractions in the experiments with $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$, 6.6×10^{-5}, 1.7×10^{-4} and 3.3×10^{-4} mol fraction. Although the nominal rhodium loading increases dramatically in this series of experiments, the pseudo steady state concentration of the intermediate is only marginally affected. As previously shown, this is due to the functional form of the interdependence $[C_6H_{11}CORh(CO)_4]_{SS} \approx K[Rh_4(CO)_{12}]_{SS}^{0.25}$.[9]

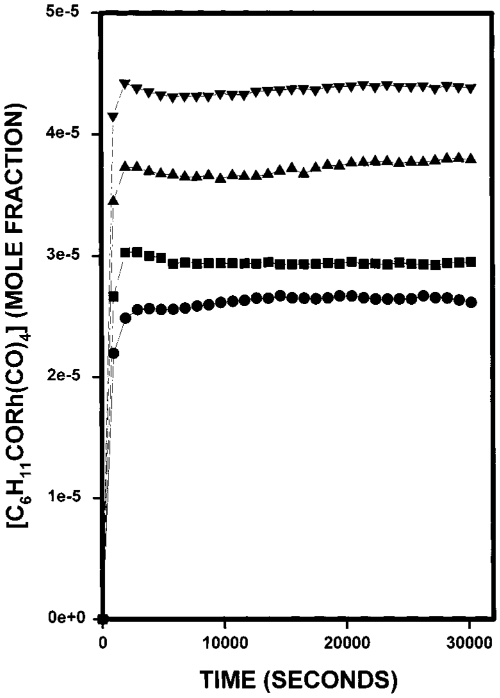

Figure 2. Time-dependent mole fraction concentrations of the acyl intermediate $C_6H_{11}CORh(CO)_4$ in the four kinetic experiments. $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$ (●), 6.6×10^{-5} (■), 1.7×10^{-4} (▲), and 3.3×10^{-4} mol fraction (▼).

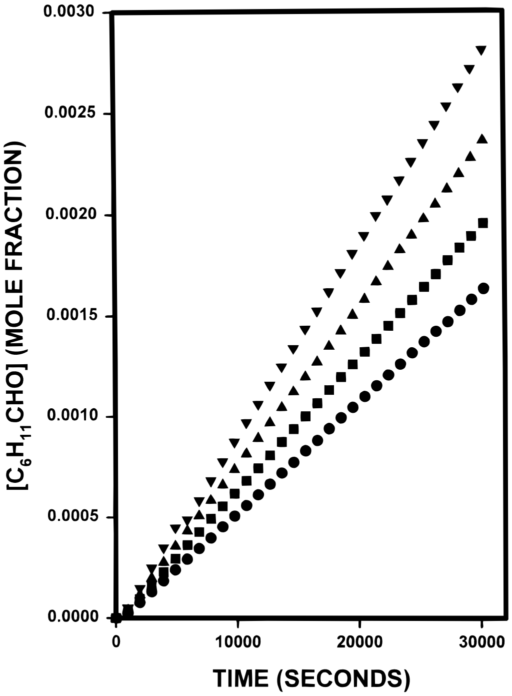

Figure 3. Time-dependent mole fraction concentrations of the aldehyde product $C_6H_{11}CHO$ in the four kinetic experiments. $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$ (●), 6.6×10^{-5} (■), 1.7×10^{-4} (▲), and 3.3×10^{-4} mol fraction (▼).

The time-dependent concentrations of the product $C_6H_{11}CHO$ are shown in Figure 3. With the exception of the first 30 min, the rates of product formation are constants. The rates are ca. 9.3×10^{-8}, 7.7×10^{-8}, 6.4×10^{-8}, and 5.3×10^{-8} (mol fraction) s^{-1} in the experiments with $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$, 6.6×10^{-5},

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(28) Davies, M. E. *Numerical Methods and Modelling for Chemical Engineers*; Wiley: New York, 1984.

(29) Shirt, R.; Garland, M.; Rippin, D. W. T. *Anal. Chim. Acta* **1998**, *374*, 67.

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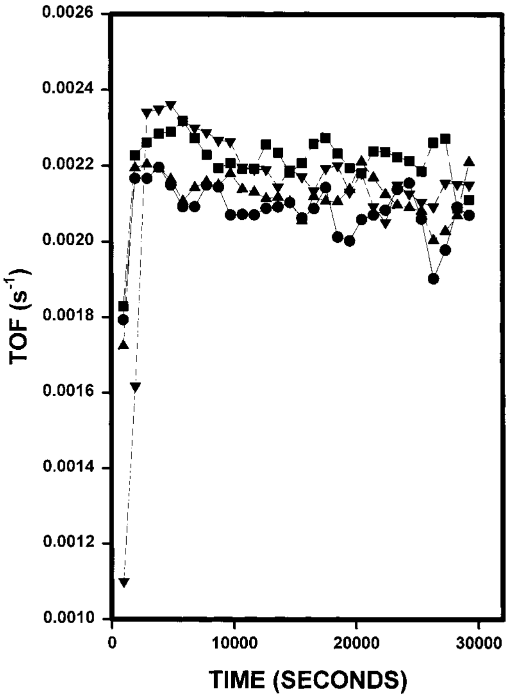

Figure 4. Time-dependent turnover frequencies in the four kinetic experiments. $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$ (●), 6.6 × 10^{-5} (■), 1.7 × 10^{-4} (▲), and 3.3 × 10^{-4} mol fraction (▼).

1.7 × 10^{-4}, and 3.3 × 10^{-4} mol fraction. The corresponding final conversions of C_6H_{10} were only 1.0, 1.3, 1.7, and 1.9%.

Kinetic Analyses. Following previous extensive studies concerning the numerical evaluation of turnover frquencies from in situ spectroscopic data,[29] the turnover freqencies in this study were evaluated using a simple central difference scheme, namely

$$\mathrm{TOF}_t = \frac{d[C_6H_{11}CHO]_t}{dt}\frac{1}{[C_6H_{11}CORh(CO)_4]_t} \quad (7)$$

The turnover frequencies for each experimental run as a function of time are shown in Figure 4. Regression of the data for each run provided the values TOF(50 mg) = (2.10 ± 0.08) × 10^{-3}, TOF(100 mg) = (2.23 ± 0.08) × 10^{-3}, TOF(250 mg) = (2.13 ± 0.08) × 10^{-3}, and TOF(500 mg) = (2.18 ± 0.16) × 10^{-3}, where the errors are listed as twice the standard deviation, i.e., the 95% confidence limit.

To evaluate the possible contribution of a catalytic binuclear elimination reaction, a plot of the TOFs versus $[Rh_4(CO)_{12}]^{0.25}$ was prepared. This plot is shown in Figure 5. Regression of the data provided the result TOF = (0.002 11 ± 0.000 06 s^{-1}) + (0.000 53 ± 0.000 62 s^{-1})$[Rh_4(CO)_{12}]^{0.25}$, where the errors are presented as twice the standard deviation.

First, since the value of k_1 is 0.002 11 ± 0.000 06 s^{-1}, the numerical value of 0.002 11 has considerable statistical significance. Second, since the value of k_2 is 0.000 53 ± 0.000 62 s^{-1}, the value of 0.000 53 s^{-1} has little, if any, statistical significance. Indeed, it is within the 95% confidence limit of 0.000 62 s^{-1}. Third, even if a catalytic binuclear elimination reaction exists, its contribution to total product formation is negligible. This is easily seen by substituting the average value $[Rh_4(CO)_{12}]^{0.25} = 0.1$ into the regression. Consequently, the leading term is 0.002 11 s^{-1} and the second term given by $k_2K_{eq}[Rh_4(CO)_{12}]^{0.25}$ is 0.000 053. If a catalytic binuclear elimination reaction does exist under the present reaction conditions, it accounts for almost certainly less than 4% of the total product formation. It should be noted that these results do not exclude the possibility of a significant contribution from a monometallic CBER under reaction conditions considerably removed from those used in this study.

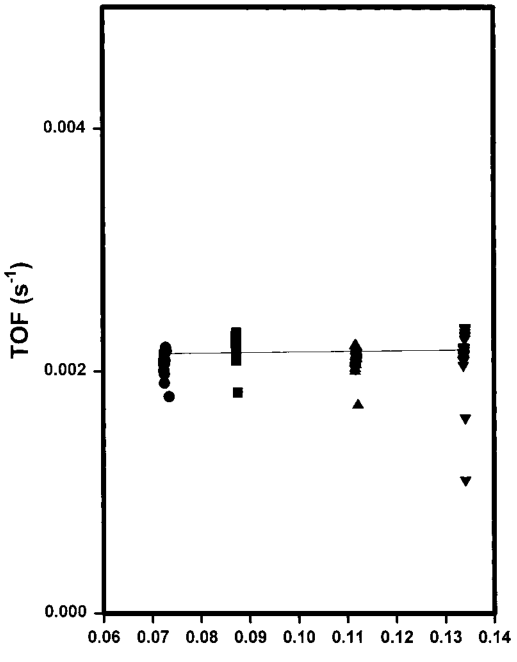

Figure 5. Dependence of TOF on the variable $[Rh_4(CO)_{12}]^{0.25}$. $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$ (●), 6.6 × 10^{-5} (■), 1.7 × 10^{-4} (▲), and 3.3 × 10^{-4} mol fraction (▼).

Conclusions

In situ spectroscopic and kinetic measurements have been made of the unmodified homogeneous rhodium-catalyzed hydroformylation of cyclohexene to cyclohexanecarboxaldehyde. A series of well-defined experiments were performed with increasing liquid-phase rhodium concentrations, holding all other parameters essentially constant. Regression of the kinetic data indicates that there is no statistically significant contribution to aldehyde formation from a catalytic binuclear elimination mechanism under the present reaction conditions. All aldehyde formation can be accounted for in terms of the hydrogenolysis of acyl rhodium tetrcarbonyl with molecular hydrogen as the rate-limiting step. This supports the classic unicyclic hydroformylation mechanism.[30]

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[30] Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; Reidel: Dordrecht, The Netherlands, 1986.