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Kinetics of the Formation and Hydrogenolysis of Acylrhodium Tetracarbonyl

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Both the formation and the hydrogenolysis of an acylrhodium tetracarbonyl $RCORh(CO)_4$ (R = $CH_2CH_2C(CH_3)_3$) have been studied during hydroformylation experiments starting with $Rh_4(CO)_{12}$ as catalyst precursor at 277–293 K in *n*-hexane as solvent. The time-dependent concentrations of all the observable species $Rh_4(CO)_{12}$, $RCORh(CO)_4$, 3,3-dimethylbut-1-ene (33DMB), and 4,4-dimethylpentanal were measured by using high-pressure in situ infrared spectroscopy. During the 8-h experiments, essentially quantitative transformation of the polynuclear catalyst precursor $Rh_4(CO)_{12}$ to the mononuclear intermediate $RCORh(CO)_4$ occurred. Only ν(M–CO) bands arising from $Rh_4(CO)_{12}$ and $RCORh(CO)_4$ could be observed in the high quality in situ infrared spectra. The formation of $RCORh(CO)_4$ was found to follow the rate expression $\text{rate(I)} = k_0(\text{I})[Rh_4(CO)_{12}]^1[CO]^{1.8}[H_2]^{0.7}[33DMB]^{0.1}$, with the apparent activation parameters $\Delta H^* = 74.4 \pm 12.0$ kJ/mol (17.8 ± 2.9 kcal/mol) and $\Delta S^* = -19.4 \pm 41.8$ J/mol K (-4.6 ± 10 cal/mol K). The results suggest (i) that there exists a preequilibrium between the catalyst precursor $Rh_4(CO)_{12}$, CO, and a species with the stoichiometry $\{Rh_4(CO)_{14}\}$ and (ii) that the activation of molecular hydrogen by $\{Rh_4(CO)_{14}\}$ is the rate-determining step in the cluster fragmentation. The continuous formation of 4,4-dimethylpentanal also occurred during the 8-h experiments. The rate of hydroformylation was proportional to the concentration of $RCORh(CO)_4$ for the duration of each experiment. The rate of hydrogenolysis of $RCORh(CO)_4$ was found to follow the expression $\text{rate(II)} = k_0(\text{II})[RCORh(CO)_4]^1[CO]^{-1.1}[H_2]^1[33DMB]^{0.1}$, with the apparent activation parameters $\Delta H^* = 49.3 \pm 4.0$ kJ/mol (11.8 ± 0.9 kcal/mol) and $\Delta S^* = 121 \pm 14$ J/mol K (29 ± 3.4 cal/mol K). The reaction orders and activation parameters are consistent with (i) a preequilibrium between the intermediate $RCORh(CO)_4$, CO, and a coordinatively unsaturated species $\{RCORh(CO)_3\}$ and (ii) the oxidative addition of molecular hydrogen to $\{RCORh(CO)_3\}$ to yield RCHO and a highly reactive metal carbonyl hydride $\{HRh(CO)_3\}$, thus supporting the classic mechanistic picture of the unmodified rhodium catalyzed hydroformylation reaction. In a much broader context, the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ represents an induction period, and the hydrogenolysis of $RCORh(CO)_4$ is a measure of the turn over frequency (TOF) for aldehyde formation. It is shown that there exists a natural separation of the overall dynamics of these hydroformylation experiments into time-dependent and time-independent terms of the form $\text{rate(II)} = [RCORh(CO)_4]_t\text{TOF}$ where $[RCORh(CO)_4] = f(x_1...x_n,T,t)$ and $\text{TOF} = f(x_1...x_n,T)$. The observed rate of hydroformylation is a highly nonlinear function in most of the reaction variables, at least for initial reaction times.

Introduction

Rhodium is considerably more active than either cobalt or iridium in the Group VIIIB (Co, Rh, Ir) homogeneously catalyzed hydroformylation reaction.[1] In its unmodified forms starting with $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ as catalyst precursors and under the typical reaction conditions of $P_{H2,CO} \geq 5.0$ MPa and $T = 70$–110 °C, rhodium rapidly and selectively transforms alkenes to aldehydes.[2] Since the initial reports concerning the activity of unmodified rhodium complexes as catalyst precursors,[3] numerous studies have focused on elucidating the mechanism of this reaction. Kinetic studies using both α and internal olefins have shown reaction orders of $a_{H2} = 1$ in hydrogen and $a_{CO} = -1$ in carbon monoxide.[4] Further, it has been reported that the activity of the systems are normally proportional to $[Rh_4(CO)_{12}]^1$ but $[Rh_4(CO)_{12}]^{1/4}$ and $[Rh_6(CO)_{16}]^{1/6}$ have also been observed, at least in hydroformylation experiments with cyclohexene.[5] However, in contrast to the well-known phosphine-modified rhodium systems,[6] the unambiguous identification of reaction intermediates in the unmodified rhodium systems has been extremely difficult. Samples taken from ethylene hydroformylations have shown (i) $[Rh(CO)_2(\mu\text{-}O_2CR)]_2$, presumably an oxidation product obtained by the reaction of trace molecular oxygen with an acyl rhodium species,[7] and (ii) a species which was tentatively assigned as an ethylrhodium tetracarbonyl but unambiguous spectra were difficult to obtain.[8] Also, so called "stoichiometric" hydroformylations starting with $Rh_4(CO)_{12}$ and carried out at 20 °C have shown the presence of $Rh_6(CO)_{16}$.[9a] The other known low-nuclearity rhodium carbonyl complexes, namely $Rh_2(CO)_8$ and $HRh(CO)_4$, have been observed in solution at elevated pressures starting with $Rh_4(CO)_{12}$,[10] but not in the presence of alkenes. Therefore, to a large extent, the present mechanistic picture of the unmodified rhodium catalyzed hydroformylation reaction has developed by analogy to the less reactive but better understood cobalt-catalyzed system.

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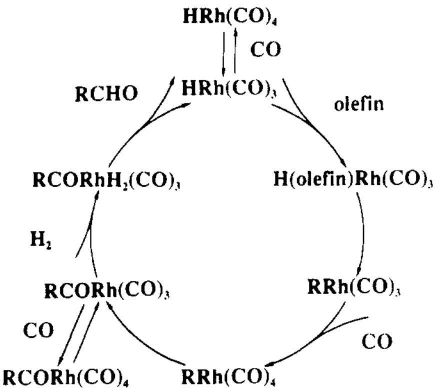

Figure 1. The classic reaction scheme for the unmodified rhodium catalyzed hydroformylation of alkenes.[2]

During unmodified cobalt catalyzed hydroformylations starting with $HCo(CO)_4$ and $Co_2(CO)_8$, reaction orders of $a_{H2} = 1$, and $a_{CO} = -1$ have been consistently observed.[11] In one of the earliest investigations using $Co_2(CO)_8$ as catalyst precursor at 70 °C and 4.0 MPa hydrogen,[12] a maximum in the rate of hydroformylation was obtained at a partial pressure of 1.0 MPa CO. At still higher partial pressures of carbon monoxide, the typical reaction orders for hydroformylation, particularly the inverse dependency on CO, were observed. Subsequent studies established that the observed reaction orders originate from the oxidative addition of molecular hydrogen to a mononuclear coordinately unsaturated acylcobalt tricarbonyl intermediate. The species $\{RCOCo(CO)_3\}$ exists in equilibrium with a considerably more stable coordinatively saturated species $RCOCo(CO)_4$ and gives rise to the reaction order $a_{CO} = -1$ due to the carbon monoxide dependence of the equilibrium.[13] Concerning the identification of cobalt intermediates, complexes such as $HCo(CO)_4$,[14] $RCo(CO)_4$ ($R = CH_3$, C_2H_5),[15] and $RCOCo(CO)_4$ ($R = CH_3$)[16] are known. In at least two cases, both $HCo(CO)_4$ and $RCOCo(CO)_4$ have been observed during hydroformylation experiments.[17,18]

The classic mechanistic scheme for the catalytic cycle of the unmodified rhodium hydroformylation reaction is shown in Figure 1.[2] Following the precedence of the analogous cobalt system, alkene activation is believed to occur via a hydride route, leading to a coordinatively saturated $18e^-$ alkyl species $RRh(CO)_4$. At this point, CO insertion takes place to generate the coordinatively unsaturated acyl species $\{RCORh(CO)_3\}$, a zero-order process with respect to dissolved CO, which undergoes hydrogenolysis to yield RCHO and a highly reactive $16e^-$ hydride $\{HRh(CO)_3\}$, thus closing the catalytic cycle. Given the aforementioned considerations, the coordinatively saturated $18e^-$ species $HRh(CO)_4$ and $RCORh(CO)_4$ assume roles outside the active cycle, but are in rapid equilibrium exchange with species residing on the catalytic cycle.

Recently, the mononuclear intermediate $RCORh(CO)_4$ ($R = \text{-}CH_2CH_2C(CH_3)_3$) was identified by high-pressure infrared spectroscopy during rhodium-catalyzed hydroformylations starting with both $CoRh(CO)_7$ and $Rh_4(CO)_{12}$ as catalyst precursors.[19] In the case of $CoRh(CO)_7$ as catalyst precursor,[20] the rapid formation of $RCORh(CO)_4$ ($R = CH_2CH_2C(CH_3)_3$) occurred under very mild conditions (293 K, 0.2 MPa CO, 0.8 MPa H_2); however, the system exhibited strong deactivation which complicated the interpretation of the observed kinetics.[21-23] With $Rh_4(CO)_{12}$ as catalyst precursor and under elevated partial pressures of CO, the slow formation of $RCORh(CO)_4$ was observed, without accompanying side reactions.[22] Under typical reaction conditions of 293 K, 2.0 MPa CO and 2.0 MPa H_2, the quantitative formation of $RCORh(CO)_4$ from $Rh_4(CO)_{12}$ occurred in a few hours. Parallel to the formation of the intermediate $RCORh(CO)_4$, the slow transformation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal was also observed, indicating the continuous hydrogenolysis of $RCORh(CO)_4$ at these temperatures. The high quality in situ infrared spectra of the active system showed $Rh_4(CO)_{12}$ and $RCORh(CO)_4$ as the only observable organometallic species, 3,3-dimethylbut-1-ene, 4,4-dimethylpentanal, *n*-hexane (solvent), and dissolved carbon monoxide. Since these initial reports, other alkenes have been used in this reaction, and the corresponding $RCORh(CO)_4$ (R = ethyl, cyclopentyl and cyclohexyl) have been observed.[24]

The observation of $RCORh(CO)_4$ starting from $Rh_4(CO)_{12}$ as catalyst precursor raises numerous question. At the most basic level, there are questions concerning the mechanism(s) by which a reduction in the nuclearity of the system (eq 1) occurs. In this regard, some systematic trends are seen in the fragmentation of metal clusters, particularly metal carbonyl clusters, under well-defined conditions.[25,26] But given the multicomponent nature of the present system, i.e. $Rh_4(CO)_{12}$, $CH_2{=}CHC(CH_3)_3$, CO, and H_2, dissolved in *n*-hexane, and given the fact that the reduction in nuclearity proceeds to a mononuclear level, additional complexities can be anticipated.

Equation 1 represents a temporal as well as a mechanistic problem. At room temperature, the catalyst precursor $Rh_4(CO)_{12}$ is not instantly transformed to $RCORh(CO)_4$. Considerable time is required to reach the maximum or steady-state concentration of intermediate(s). This time interval represents an induction period in the overall hydroformylation kinetics.[27,28] In this respect, the

$$Rh_4(CO)_{12} + 8CO + 2H_2 + 4CH_2{=}CHC(CH_3)_3 \rightarrow 4RCORh(CO)_4 \quad (1)$$

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(27) There are actually two distinct *relaxation* processes involved in the present study, these are (A) the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ and (B) the relaxation of all the intermediates, including the unobservable species such as $\{HRh(CO)_3\}$ and $RRh(CO)_4$, to their respective local steady-state concentrations. Relaxation A is orders of magnitude slower than relaxation B.

present case of unmodified rhodium catalyzed hydroformylation differs significantly from the well-known phosphine-modified case. In the latter case,[29–31] the catalyst precursors such as $ClRh(CO)(PPh_3)_2$ are mononuclear from the start, and at most, only a few elementary steps are required to transform the precursors to intermediates.

At another level, the hydrogenolysis of $RCORh(CO)_4$ is the single most important mechanistic point concerning the steady state hydroformylation kinetics of the unmodified rhodium catalyzed reaction. The existence of $RCORh(CO)_4$ as the predominant intermediate under reaction conditions suggests that the turn over limiting step of the catalytic cycle soon follows. Given the previously reported reaction orders for unmodified cobalt and rhodium systems, the nonelementary hydrogenolysis of $RCORh(CO)_4$ is represented as shown in eq 2. The hydrogenolysis of two other acylmetal complexes, notably $RCOCo(CO)_4$[32] and $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$,[33] have been studied in considerable detail. In the latter cases, the complexes can be isolated, thus facilitating a rather straightforward experimental approach. Such an option is not available in the case of $RCORh(CO)_4$. In this paper, the reaction orders and apparent activation parameters are presented for both the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ (reaction I) and the hydrogenolysis of $RCORh(CO)_4$ (reaction II). The measurements were carried out by using high-pressure infrared spectroscopy as the quantitative in situ method. Relatively few in situ infrared studies of active homogeneously catalyzed systems have appeared in the open literature,[17,18,34,35] and the majority of these have been concerned with the identification of intermediates rather than analysis of the overall time dependence of the systems. In this regard, the present work presents a systematic approach to understanding and interpreting the often complex kinetics of homogeneously catalyzed systems, by making explicit use of the time-dependent transformation of the catalyst precursor.

$$RCORh(CO)_4 \overset{-CO}{\rightleftharpoons} \{RCORh(CO)_3\} \overset{H_2}{\rightleftharpoons} \{HRh(CO)_3\} + RCHO \quad (2)$$

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern) or argon (99.998%, Pan Gas, Luzern) atmosphere by using standard Schlenk techniques.[36] $Rh_4(CO)_{12}$ was purchased from Strem Chemicals (Newburyport, MA), and was used as obtained. Puriss quality *n*-hexane (Fluka AG, Buchs) was refluxed from sodium potassium alloy under nitrogen. 3,3-Dimethylbut-1-ene (Fluka AG, Buchs) was degassed and stored over molecular sieve. Reactions were carried out with carbon monoxide which was produced at the ETH-Z (and stored in aluminum cylinders), and hydrogen 99.999% (Pan Gas, Luzern).

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 6-bladed turbines in both the gas and liquid phases (Autoclave Engineer, Erie) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK30, Orlita AG, BRD) with a maximum rating of 32.5 MPa and 3 L per hour 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, Erie). The entire system (autoclave, transfer lines, and infrared cell) was cooled by using a Lauda RX20 (Austria) cryostat and could be maintained isothermal (ΔT = 0.5 °C) in the range of −20 °C 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, Wintertur). The piezocrystals were periodically calibrated on a Haenni PDG 022 calibration bench (Stuttgart, FRG). The entire system was gas-tight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Z of SS316 steel and could be heated or cooled. The NaCl (Korth, BRD), KBr (Korth, FRG), and single-crystal silicon (ETH-Zürich) windows 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[37a] is a variation on a design due to Noack[37b] and differs in some respects with other high-pressure infrared cells described in the literature (for a review see Whyman[37g]). The high-pressure cell was situated in a Perkin-Elmer PE983 infrared spectrophotometer equipped with a Model 3600G data station. Spectra were recorded with a 0.22-mm slit width. Details of the equipment and IR cell can be found elsewhere.[22]

The tetranuclear carbonyl $Rh_4(CO)_{12}$ has absorbance maxima at 2074, 2068, 2061, 2043, and 1885 cm^{-1} in the infrared,[38] and the mononuclear intermediate $RCORh(CO)_4$ ($R = CH_2CH_2C(CH_3)_3$) has absorbance maxima at 2111, 2065, 2039, 2020, and 1698 cm^{-1}.[19] The extinction coefficient of $Rh_4(CO)_{12}$ at 1885 cm^{-1} (bridging CO) is $\epsilon(1885)$ = 9800 L/(mol cm) when a slit width of 0.22 mm is used. The extinction coefficient of *n*-hexane at 1138 cm^{-1} (CH_2 vibrations)[39] is $\epsilon(1138)$ = 2.353 L/(mol cm), also at a slit width of 0.22 mm. 3,3-Dimethylbut-1-ene and 4,4-dimethylpentanal have absorbance at 1642 cm^{-1} (C=C stretching mode)[39] and 1734 cm^{-1} (C=O stretching mode),[39] respectively, and the corresponding extinction coefficients are $\epsilon(1642)$ = 50 L/(mol cm) and $\epsilon(1734)$ = 360 L/(mol cm).

Kinetic Studies. $Rh_4(CO)_{12}$ (37 mg, 5 × 10^{-5} mol) was dissolved in 200 ml of *n*-hexane (1.51 mole) in a Schlenk tube under a nitrogen atmosphere, 3,3-dimethylbut-1-ene 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

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stirring (200 rpm), carbon monoxide (1.0–4.0 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 40 min. Initial in situ infrared spectra were then taken from 2200–1600 cm^{-1} (M–CO range) and from 1300–1100 cm^{-1} (hexane). The initial spectra show that the reagents $Rh_4(CO)_{12}$, CO, and $CH_2{=}CH\text{-}C(CH_3)_3$ can be clearly identified and that no measurable reaction has occurred. Little to no 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 (0.5–3.0 MPa) was added to the system. After 8 h, the experiments were stopped. The spectra were analyzed after the end of the 8-h reaction period and not online.

Four sets of experiments were performed. In each set of experiments, one experimental parameter was systematically varied while holding the remaining variables essentially constant. In this manner, variations in the concentrations of 3,3-dimethylbut-1-ene, dissolved hydrogen, and dissolved carbon monoxide and variations in temperature were studied. The initial reaction conditions of the "reference" experiment were 1.51 mol of *n*-hexane, 5×10^{-5} mol of $Rh_4(CO)_{12}$ (3.25×10^{-4} mol fraction), 0.039 mol of 3,3-dimethylbut-1-ene (0.024 mol fraction), 2.0 MPa hydrogen (0.017 mol fraction), and 2.0 MPa carbon monoxide (0.033 mol fraction) at 293 K. From this reference condition, experiments were conducted by varying (i) the initial concentration of 3,3-dimethylbut-1-ene (0.012, 0.046, 0.068 mol fraction), (ii) the partial pressure of hydrogen (0.5, 1.0, 3.0 MPa), (iii) the partial pressure of carbon monoxide (1.0, 3.0, 4.0 MPa), and (iv) the reaction temperature (287, 283, 277 K). In any single experiment, less than 0.02 mol of conversion of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal occurred. The partial pressures of hydrogen and carbon monoxide in the closed batch autoclave changed less than 5% during the 8-h experiments. This partial pressure change was considered negligible, and therefore, the liquid-phase concentrations of the two gaseous components were treated as constants for the duration of each experiment.

Notation

The IUPAC suggested nomenclature for reactions and the specification of reaction parameters is observed,[40] i.e. ν_i the for stoichiometry of the ith reactant, a_i for the reaction order etc. The kinetics of two reaction schemes (I) the formation of $RCORh(CO)_4$ and (II) the hydrogenolysis of $RCORh(CO)_4$ are considered in the present study. There is an entire set of reaction parameters associated with each of these reactions, i.e., $\{\nu_i, a_i, E_a, \Delta H^{\ddagger}, \Delta S^{\ddagger}, \Delta V^{\ddagger}\}$. Thus, each reaction parameter such as a_i represents a macroscopic or observable property of one of the overall reaction sequences. Descriptive notation, such as a_i(I) and a_i(II), is used to facilitate the unambiguous discussion of the reaction parameters associated with reaction I, and reaction II.

Calculations

Reactant Concentrations. The time-dependent in situ concentrations of $Rh_4(CO)_{12}$, 3,3-dimethylbut-1-ene (33DMB), and 4,4-dimethylpentanal (44DMP) were calculated by using the characteristic infrared absorbencies at 1885, 1642, and 1734 cm^{-1}, respectively. At the end of each hydroformylation experiment, a program was executed to subtract the hexane absorbance from each spectrum (2200–1600 cm^{-1}) and to calculate the concentration of the above components. In eq 3, x_i are mole fractions, A_i are measured in situ absorbencies, B is the ratio of moles hexane n_{hex} to total moles in the liquid phase, and ϵ_i are extinction coefficients. The parameter B is defined in eq 4. In situ measurements of both the *i*-th component absorbance as well as the absorbance of *n*-hexane (1138 cm^{-1}) were needed for the calculation of liquid-phase concentrations. The numerical values of the parameters B were 0.94–0.90. Since $(n_{33DMB})_0 = (n_{33DMB})_t + (n_{44DMP})_t$, the parameter B was calculated from the initial reaction conditions for each experiment and remained constant for the duration of each experiment.

$$x_i = B(A_i\epsilon_{1138})/(A_{1138}\epsilon_i) \tag{3}$$

$$B = n_{hex}/(n_{hex} + n_{33DMB} + n_{CO} + n_{H2} + n_{44DMP}) \tag{4}$$

Concentrations of RCORh(CO)$_4$. The time-dependent concentration of the intermediate $RCORh(CO)_4$ was calculated from a mass balance over rhodium (eq 5).

$$[RCORh(CO)_4]_t = 4[Rh_4(CO)_{12}]_0 - 4[Rh_4(CO)_{12}]_t \tag{5}$$

There was a continuous one-to-one relationship between the intensity of the $RCORh(CO)_4$ bands and the calculated concentration for the duration of each experiment. There was never an indication that the mass balance did not hold. Indeed, (i) there were no observable ν(M–CO) absorbencies other than those belonging to $Rh_4(CO)_{12}$ and $RCORh(CO)_4$, (ii) there were no base line shifts in the infrared spectra which could be attributed to the decomposition of the organorhodium complexes, (iii) the solutions after reaction were transparent and brilliant yellow in color and there was no light scattering indicative of colloidal particles, and (iv) there was absolutely no indication of the decomposition of the rhodium complexes either on the walls of the reactor or on the infrared windows.

Rates of Reactions. The rates of reaction, for the transformation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal were calculated by using a finite difference equation (eq 6). This expression provides a numerical

$$(d[44DMP]/dt)_t = ([44DMP]_{t+1} - [44DMP]_{t-1})/2\Delta t \tag{6}$$

value for the rate of hydroformylation at a time t, based on the measured in situ concentrations of 4,4-dimethylpentanal at times $t - 1$ and $t + 1$. The time interval between t and $t - 1$ or $t + 1$ was 40 min, the interval between spectra. This central difference expression was chosen since it provides an accurate approximation of derivatives from sets of smooth monotonically increasing or decreasing experimental data.[41]

Solubilities. The Henry constants for hydrogen and carbon monoxide were calculated by using equations 7 and 8, respectively, where the temperature T is Kelvin degrees and where P_{sat} is the saturated vapor pressure of the *n*-hexane.[42a] The derivation of the temperature-dependent

$$\ln (H_{H2}/P_{sat}) = -1.46 + 2840/T \tag{7}$$

$$\ln (H_{CO}/P_{sat}) = -4.96 + 4050/T \tag{8}$$

form of these Henry constants can be found in the literature.[42b] These equations are strictly valid only for pure hexane in the limit of low partial pressures (specifically 0.1 MPa). However, these equations were used without further modification in the present experiments involving *dilute* solutions of 3,3-dimethylbut-1-ene in *n*-hexane. Further, the Krichevsky–Kasarnovsky equation was not used to correct for the small change in the Henry constants due to total pressure effects (2.5–6.0 MPa).[42c] Finally, both dissolved hydrogen and dissolved carbon monoxide were

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(40) (a) IUPAC *Pure Appl. Chem.* **1979**, *51*, 1. (b) IUPAC *Pure Appl. Chem.* **1989**, *61*, 23. (c) IUPAC *Pure Appl. Chem.* **1989**, *61*, 57.

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

(42) (a) Gallant, R. W. *Physical Properties of Hydrocarbons*; Gulf: Houston, 1968. (b) Jonah, D. A. *Fluid Phase Equilib.* **1983**, *15*, 173. (c) Krichevsky, I. R.; Kasarnovsky, T. S. *J. Am. Chem. Soc.* **1935**, *67*, 2168. (d) In terms of short term transient effects, the liquid phase is essentially saturated with dissolved gas in 1–2 min.

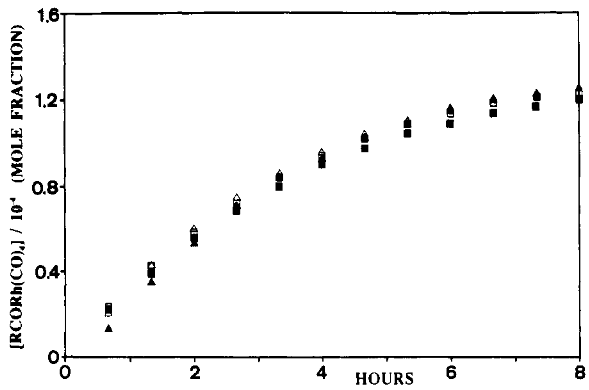

Figure 2. Effect of the initial 3,3-dimethylbut-1-ene concentration on the formation of $RCORh(CO)_4$ as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.018 mol fraction H_2 (2.0 MPa), in *n*-hexane at 293 K. Symbols are as follows: △, $x_{33DMB} = 0.012$; ■, $x_{33DMB} = 0.024$; ◆, $x_{33DMB} = 0.046$; □, $x_{33DMB} = 0.068$.

considered to be ideal solutes. No mixing rules were invoked in order to compensate for nonideality in the two-phase system.[42d]

Results

3,3-Dimethylbut-1-ene Concentration. The initial concentration of 3,3-dimethylbut-1-ene was systematically varied in four hydroformylation experiments performed at 293 K, 2.0 MPa hydrogen, and 2.0 MPa carbon monoxide. The initial concentrations of 3,3-dimethylbut-1-ene in mole fractions were x_{33DMB} = 0.012, 0.024, 0.046, and 0.068. The corresponding initial concentrations of $Rh_4(CO)_{12}$, as measured by in situ IR in solution, were $[Rh_4(CO)_{12}]_0 = 3.69 \times 10^{-5}$, 3.29×10^{-5}, 3.50×10^{-5}, and 3.36×10^{-5} mol fraction.

There was no indication of fragmentation (for example to $Rh_2(CO)_8$, ν(M–CO) = 2086, 2061, 1860, and 1845 cm^{-1})[10a,b] nor degradation (for example ligand substitution) of the metal carbonyl cluster $Rh_4(CO)_{12}$ before the addition of hydrogen. Further, the catalyst precursor was essentially free of $Rh_6(CO)_{16}$ (2105, 2070(s), 2047, 2040, 2022, 2020, 1833, and 1793(s) cm^{-1}),[43] a common impurity.

The concentration of $RCORh(CO)_4$ as a function of reaction time for the four experiments is presented in Figure 2. In these 8-h experiments, essentially quantitative conversion of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ has occurred, and the rate of formation of $RCORh(CO)_4$ is virtually independent of the initial concentration of 3,3-dimethylbut-1-ene. The smooth, monotonically increasing kinetic curves are a direct consequence of the isothermal and isobaric conditions of the in situ measurements, as opposed to sampling techniques.[44]

For the duration of each reaction, the in situ infrared spectra showed ν(M–CO) vibrations from only $Rh_4(CO)_{12}$ and $RCORh(CO)_4$. A spectrum representing approximately 65% conversion of $Rh_4(CO)_{12}$, and about 10% conversion of alkene, is shown in Figure 3. The ν(M–COR) band of the acylrhodium tetracarbonyl is clearly visible at $\nu \approx 1700$ cm^{-1}. In comparison, the ν(M–COR) band in the unmodified cobalt case occurs at $\nu \approx 1720$ cm^{-1},[45a] and the ν(M–COR) band in the modified rhodium case occurs

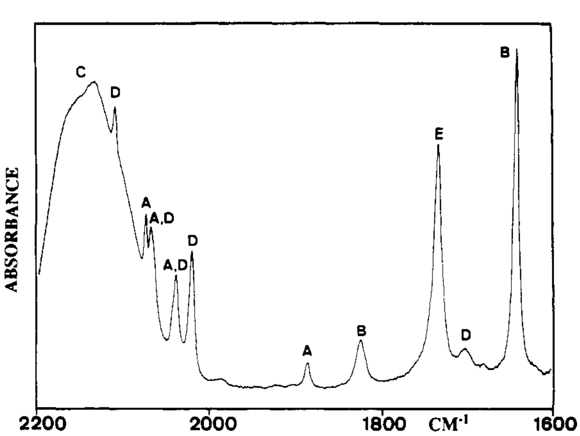

Figure 3. High-pressure in situ infrared spectrum of a hydroformylation solution after 4.7 h of reaction (*n*-hexane subtraction). Conditions were 3.29 × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), 0.034 mol fraction CO (2.0 MPa), 0.018 mol fraction H_2 (2.0 MPa), in *n*-hexane at 293 K. Peaks are as follows: A, $Rh_4(CO)_{12}$; B, 3,3-dimethylbut-1-ene; C, dissolved carbon monoxide; D, $RCORh(CO)_4$; E, 4,4-dimethylpentanal.

at $\nu \approx 1645$ cm^{-1}.[45b–d] Also, due to the partial overlap of $Rh_4(CO)_{12}$ and $RCORh(CO)_4$ absorbencies, the bands at $\nu \approx 2067$ cm^{-1} and $\nu \approx 2043$ cm^{-1} appear asymmetric. An infrared spectrum of the intermediate $RCORh(CO)_4$ as well as an analysis of the band structure has appeared.[19]

By assuming that the transformation is first order in the metal carbonyl cluster $Rh_4(CO)_{12}$, the formation of $RCORh(CO)_4$ can be analyzed by using equations 9–11.

$$d[Rh_4(CO)_{12}]/dt = -k[Rh_4(CO)_{12}][33DMB]^{a} \quad (9)$$

$$\ln([Rh_4(CO)_{12}]_t/[Rh_4(CO)_{12}]_0) = -k[33DMB]_0^{a}t \quad (10)$$

$$k_{obs}(I) = k[33DMB]_0^{a} \quad (11)$$

Recognizing that relatively low conversions of 3,3-dimethylbut-1-ene have occurred in the experiments (7–38%), it is convenient to treat the alkene concentrations as constants for the duration of each experiment, and to use the initial concentrations $[33DMB]_0$ in the rate expressions. This latter simplification has a minor effect on the numerical results, since as will be shown, $a_{33DMB}(I)$ approaches 0 in the present concentration regime.

Applying eq 10 to the experimentally measured concentrations of $Rh_4(CO)_{12}$ gave straight lines over 3 half-lives for all data sets, confirming that the formation of $RCORh(CO)_4$ is first order in $Rh_4(CO)_{12}$. The rate constants $k_{obs}(x_{33DMB})$ are $k_{obs}(0.012) = (7.1 \pm 0.05) \times 10^{-5}$ s^{-1}, $k_{obs}(0.024) = (8.2 \pm 0.14) \times 10^{-5}$ s^{-1}, $k_{obs}(0.046) = (8.5 \pm 0.21) \times 10^{-5}$ s^{-1}, and $k_{obs}(0.068) = (8.8 \pm 0.14) \times 10^{-5}$ s^{-1}. The observed reaction order is $a_{33DMB}(I) = 0.11 \pm 0.02$.

The time-dependent concentrations of the hydroformylation product 4,4-dimethylpentanal are shown in Figure 4. The variation in the initial concentration of 3,3-dimethylbut-1-ene has little effect on the rate of formation of 4,4-dimethylpentanal. The conversions of alkene at the end of the 8-h experiments were 0.0045–0.0055 mole fractions for the experiments starting with x_{33DMB} = 0.012, 0.024, 0.046, and 0.068 corresponding to conversions of 38.3, 20.0, 9.5, and 7.7%, respectively.

A characteristic increase in the rate of hydroformylation as a function of time is seen in Figure 4. The rate of hydrogenolysis rises until a fixed maximum hydroformylation rate is reached. This time-dependent hydroformylation behavior reflects the noninstantaneous transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ and represents an induction period.

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(43) Chini, P. *J. Chem. Soc., Chem. Comm.* **1967**, 440.

(44) Upon sampling, the present system undergoes recombination to $Rh_4(CO)_{12}$ on the time scale of about 5 min or less.[27,28]

(45) (a) Marko, L.; Bor, G.; Almasy, G.; Szabo, P. *Brennst.-Chem.* **1963**, *44*, 184. (b) Keim, W. *J. Organomet. Chem.* **1969**, *19*, 161. (c) Yagupsky, G.; Brown, C. K.; Wilkinson, G. *J. Chem. Soc., Chem. Comm.* **1969**, 1244. (d) Yagupsky, G.; Brown, C. K.; Wilkinson, G. *J. Chem. Soc.*, **1970**, 1392.

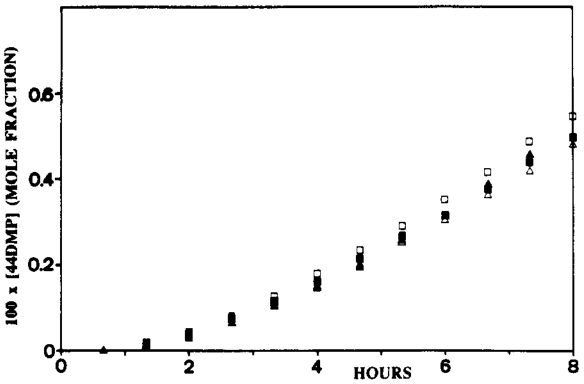

Figure 4. Effect of the initial 3,3-dimethylbut-1-ene concentration on the formation of RCHO as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.018 mol fraction H_2 (2.0 MPa), in *n*-hexane at 293 K. Symbols are as follows: △, $x_{33DMB} = 0.012$; ■, $x_{33DMB} = 0.024$; ▲, $x_{33DMB} = 0.046$; □, $x_{33DMB} = 0.068$.

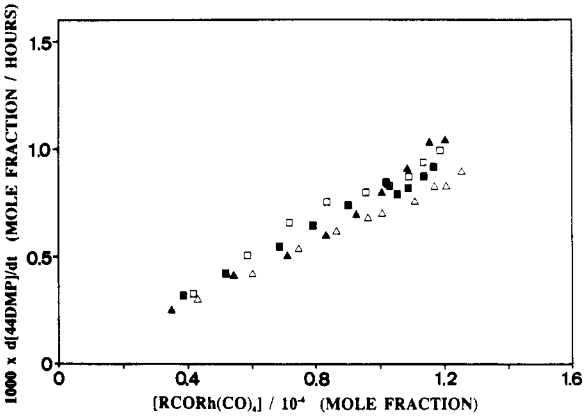

Figure 5. Effect of the initial 3,3-dimethylbut-1-ene concentration on the rate constant k_{obs}(II) for the formation of RCHO. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.018 mol fraction H_2 (2.0 MPa), in *n*-hexane at 293 K. Symbols are as follows: △, $x_{33DMB} = 0.012$; ■, $x_{33DMB} = 0.024$; ▲, $x_{33DMB} = 0.046$; □, $x_{33DMB} = 0.068$.

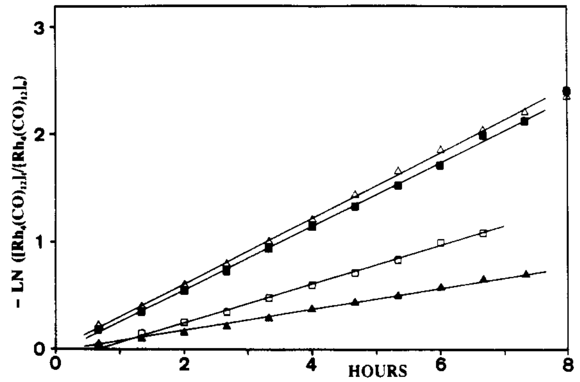

Figure 6. Effect of the liquid phase hydrogen concentration on the rate constant k_{obs}(I) for formation of $RCORh(CO)_4$. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: ▲, $x_{H2} = 0.0045$; □, $x_{H2} = 0.0089$; ■, $x_{H2} = 0.018$; △, $x_{H2} = 0.027$.

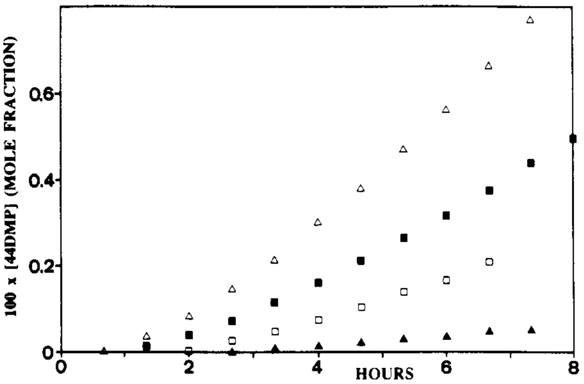

Figure 7. Effect of the liquid-phase hydrogen concentration on the formation of RCHO as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: ▲, $x_{H2} = 0.0045$; □, $x_{H2} = 0.0089$; ■, $x_{H2} = 0.018$; △, $x_{H2} = 0.027$.

The rate of formation of 4,4-dimethylpentanal is equal to the rate of hydrogenolysis of $RCORh(CO)_4$ (eq 2). In eq 12, the rate of formation of 4,4-dimethylpentanal is set proportional to the concentration of $RCORh(CO)_4$, where both terms, the rate, and the concentration are time dependent. The rate constant k_{obs}(II) is pseudo-first-order

$$(\mathrm{d}[44\mathrm{DMP}]/\mathrm{d}t)_t = k_{\mathrm{obs}}(\mathrm{II})[\mathrm{RCORh(CO)_4}]_t \qquad (12)$$

and has units of reciprocal time. Furthermore, k_{obs}(II) is in fact a turn over frequency (TOF) based on a mass balance for the rhodium in the active system.

The finite difference form for the rate of formation of 4,4-dimethylpentanal (eq 6) was evaluated from the data presented in Figure 4. The time-dependent rate of formation of 4,4-dimethylpentanal is proportional to the concentration of $RCORh(CO)_4$ as shown in Figure 5. The rate constants $k_{obs}(x_{33DMB})$ are $k_{obs}(0.012) = (1.96 \pm 0.06) \times 10^{-3}\ s^{-1}$, $k_{obs}(0.024) = (2.18 \pm 0.05) \times 10^{-3}\ s^{-1}$, $k_{obs}(0.046) = (2.45 \pm 0.16) \times 10^{-3}\ s^{-1}$, and $k_{obs}(0.068) = (2.26 \pm 0.09) \times 10^{-3}\ s^{-1}$. The rate constants indicate a very small dependence of the hydroformylation rate on the concentration of 3,3-dimethylbut-1-ene. If the concentrations of 3,3-dimethylbut-1-ene are treated as constants and set equal to their respective initial values $[33DMB]_0$, a reaction order $a_{33DMB}(II) = 0.1 \pm 0.05$ is obtained.

Hydrogen Concentration. Four different experiments were performed in order to examine the influence of hydrogen. These experiments were conducted at 293 K under 2.0 MPa carbon monoxide and at an initial concentration of $x_{33DMB} = 0.024$. The concentrations of hydrogen in these experiments were $x_{H2} = 0.0045$, 0.0089, 0.018, and 0.027 at hydrogen partial pressures of 0.5, 1.0, 2.0, and 3.0 MPa, respectively, and the corresponding initial concentrations of $Rh_4(CO)_{12}$ were $[Rh_4(CO)_{12}]_0 = 3.69 \times 10^{-5}$, 3.48×10^{-5}, 3.29×10^{-5}, and 3.38×10^{-5} mole fraction.

The time-dependent concentrations of $Rh_4(CO)_{12}$ were transformed by using eq 10. The results are presented in Figure 6 where straight lines are obtained, indicating that the rates are first order in the metal carbonyl cluster $Rh_4(CO)_{12}$ for all data sets. The observed rate constants $k_{obs}(x_{H2})$ were $k_{obs}(0.0045) = (2.83 \pm 0.06) \times 10^{-5}\ s^{-1}$, $k_{obs}(0.0089) = (4.77 \pm 0.13) \times 10^{-5}\ s^{-1}$, $k_{obs}(0.018) = (8.17 \pm 0.14) \times 10^{-5}\ s^{-1}$, and $k_{obs}(0.027) = (8.1 \pm 0.07) \times 10^{-5}\ s^{-1}$. The experimentally determined reaction order in hydrogen for the formation of $RCORh(CO)_4$ from $Rh_4(CO)_{12}$ is $a_{H2}(I) = 0.7 \pm 0.1$.[46a]

The liquid-phase concentration of hydrogen had a strong influence on the rate of hydrogenolysis of $RCORh(CO)_4$

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(46) (a) Total pressure as well as liquid phase mole fraction was varied simultaneously in this series of experiments. However, the small total pressure variation used in this series will have a negligible effect on the interpretation of the data. (b) An activation volume of $\Delta V^{*} = -20$ mL/mol has been measured for the oxidative addition of molecular hydrogen in solution to *trans*-$IrCl(CO)(PPh_3)_2$. Schmidt, R.; Geis, M.; Kelm, H. *Z. Phys. Chem.* (*Munich*) 1974, *92*, 223.

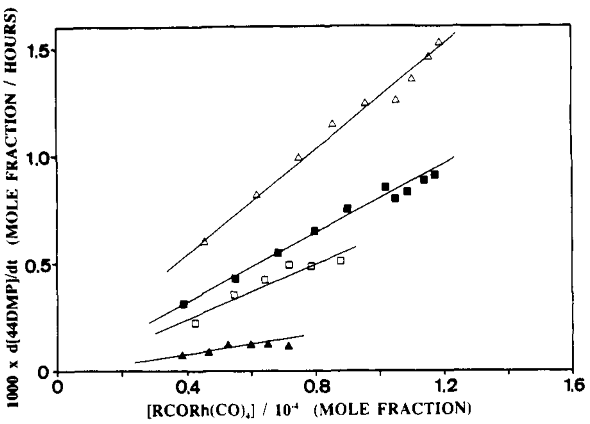

Figure 8. Effect of the liquid phase hydrogen concentration on the rate constant $k_{obs}(II)$ for formation of RCHO. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.034 mol fraction CO (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: ▲, x_{H2} = 0.0045; □, x_{H2} = 0.0089; ■, x_{H2} = 0.018; △, x_{H2} = 0.027.

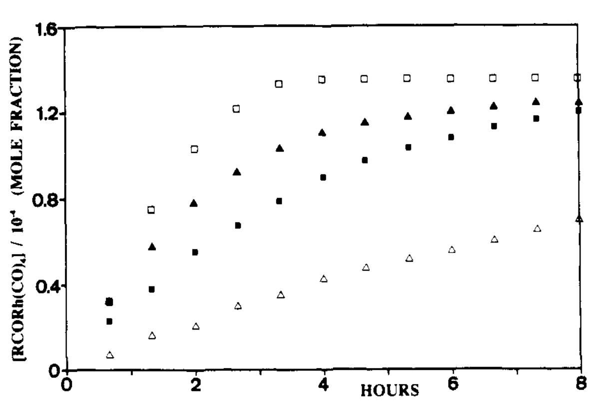

Figure 9. Effect of the liquid phase carbon monoxide concentration on the formation of $RCORh(CO)_4$ as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), 0.018 mol fraction H_2 (2.0 MPa) in *n*-hexane at 293 K. Symbols are as follows: △, x_{CO} = 0.017; ■, x_{CO} = 0.034; ▲, x_{CO} = 0.051; □, x_{CO} = 0.068.

for initial reaction times as shown in Figure 7. The rate of formation of 4,4-dimethylpentanal increases with increasing hydrogen pressure, and the characteristic "induction" curves are seen. Evaluating the time-dependent rates gives the results presented in Figure 8. Straight lines are obtained, showing that the rate is first order in $RCORh(CO)_4$ at all the hydrogen pressures studied. The evaluated rate constants $k_{obs}(x_{H2})$ are $k_{obs}(0.0045)$ = (5.20 ± 0.58) × 10^{-4} s^{-1}, $k_{obs}(0.0089)$ = (1.76 ± 0.11) × 10^{-3} s^{-1}, $k_{obs}(0.018)$ = (2.18 ± 0.03) × 10^{-3} s^{-1}, and $k_{obs}(0.027)$ = (3.45 ± 0.13) × 10^{-3} s^{-1}, and the reaction order in hydrogen for the rate of hydrogenolysis of $RCORh(CO)_4$ is $a_{H2}(II)$ = 1.0 ± 0.2.[46a,b] The conversions of 3,3-dimethylbut-1-ene in these experiments after 8 h of reaction were 2, 10.4, 18.3, and 32% at x_{H2} = 0.0045, 0.0089, 0.018, and 0.027, respectively.[47]

Carbon Monoxide Concentrations. Four experiments were performed in order to study the influence of carbon monoxide. These experiments were conducted at 293 K under 2.90 MPa hydrogen and at an initial concentration of x_{33DMB} = 0.024. The concentration of dissolved carbon monoxide in the experiments were x_{CO} = 0.017, 0.034, 0.051, and 0.068 at 1.0, 2.0, 3.0, and 4.0 MPa carbon monoxide, and the corresponding initial concentrations of $Rh_4(CO)_{12}$ in mole fractions were $[Rh_4(CO)_{12}]_0$ = 3.52 × 10^{-5}, 3.30 × 10^{-5}, and 3.06 × 10^{-5}, and 3.55 × 10^{-5}.

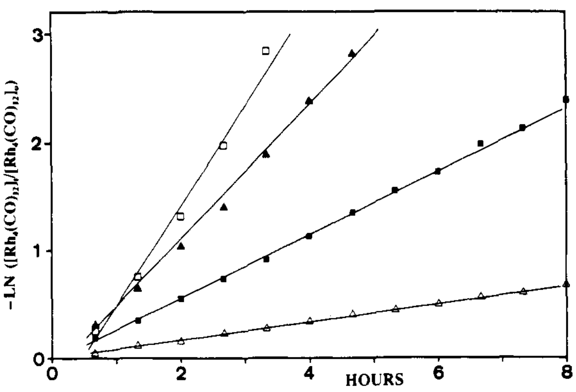

Figure 10. Effect of the liquid-phase carbon monoxide concentration on the rate constant $k_{obs}(I)$ for formation of $RCORh(CO)_4$. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.018 mol fraction H_2 (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: △, x_{CO} = 0.017; ■, x_{CO} = 0.034; ▲, x_{CO} = 0.051; □, x_{CO} = 0.068.

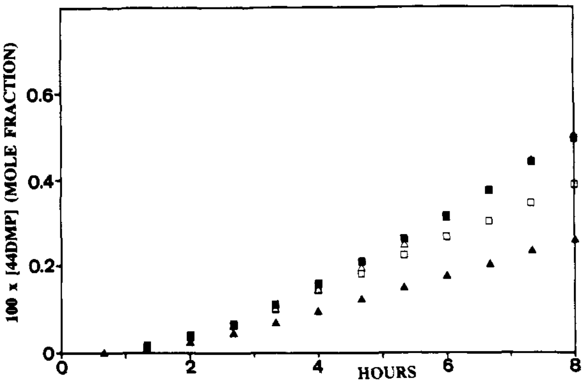

Figure 11. Effect of the liquid phase carbon monoxide concentration on the formation of RCHO as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.018 mol fraction H_2 (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: △, x_{CO} = 0.017; ■, x_{CO} = 0.034; ▲, x_{CO} = 0.051; □, x_{CO} = 0.068.

The influence of carbon monoxide on the formation of $RCORh(CO)_4$ is shown in Figure 9. The concentration of carbon monoxide had a very strong influence on the rate of formation of $RCORh(CO)_4$. At 1.0 MPa, only 50% conversion was achieved at the end of 8 h, whereas at 4.0 MPa, 50% conversion was achieved in approximately 1 h. Taking the natural logarithm of the corresponding $Rh_4(CO)_{12}$ concentration data leads to the results presented in Figure 10. Straight lines are obtained for all data sets. The observed rate constants $k_{obs}(x_{CO})$ are $k_{obs}(0.017)$ = (2.36 ± 0.04) × 10^{-5} s^{-1}, $k_{obs}(0.034)$ = (8.17 ± 0.14) × 10^{-5} s^{-1}, $k_{obs}(0.051)$ = (1.65 ± 0.06) × 10^{-4} s^{-1}, and $k_{obs}(0.068)$ = (2.39 ± 0.21) × 10^{-4} s^{-1}. The reaction order in carbon monoxide for the formation of acylrhodium tetracarbonyl is $a_{CO}(I)$ = 1.75 ± 0.1. As in the previous series of experiments under hydrogen, not only mole fraction but also total pressure varies from experiment to experiment, and again total pressure effects are considered negligible.

The overall effect of carbon monoxide on the rate of formation of 4,4-dimethylpentanal is shown in Figure 11. In general, the rate of hydroformylation tends to decrease

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(47) Conversion is very sensitive to variations in the liquid phase hydrogen concentration at initial reaction times. This is due to the hydrogen dependence of the cluster fragmentation ($a_{H2}(I)$ = 0.7) coupled with the hydrogen dependence of hydrogenolysis ($a_{H2}(II)$ = 1).

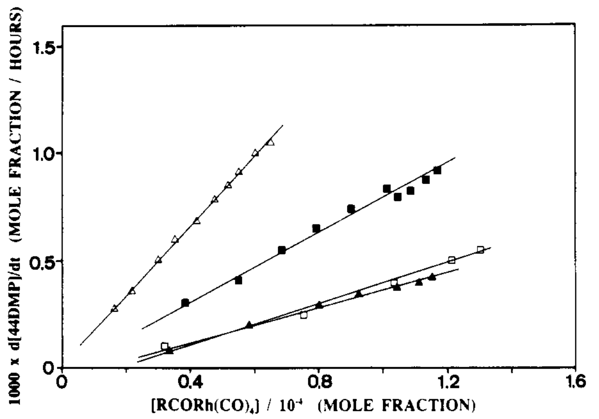

Figure 12. Effect of the liquid phase carbon monoxide concentration on the rate constant k_{obs}(II) for formation of RCHO. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.018 mol fraction H_2 (2.0 MPa), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), in *n*-hexane at 293 K. Symbols are as follows: △, x_{CO} = 0.017; ■, x_{CO} = 0.034; ▲, x_{CO} = 0.051; □, x_{CO} = 0.068.

with increasing carbon monoxide concentrations; however, this does not seem to be the only effect present. There appears to be little or no change in the net hydroformylation rate between 1.0–2.0 MPa CO. This behavior can be compared to the maximum observed by Natta et al. for the unmodified cobalt catalyzed hydroformylation reaction at 1.0 MPa CO,[12] and by Marko et al. for the unmodified rhodium catalyzed hydroformylation reaction at 4.0 MPa CO at 70 °C.[4]

Figure 12 shows a plot of the rate of formation of 4,4-dimethylpentanal versus the concentration of $RCORh(CO)_4$. There is a linear dependence for all the CO data sets. The observed rate constants $k_{obs}(x_{CO})$ are $k_{obs}(0.017) = (4.46 \pm 0.6) \times 10^{-3}\ s^{-1}$, $k_{obs}(0.034) = (2.18 \pm 0.03) \times 10^{-3}\ s^{-1}$, $k_{obs}(0.051) = (9.98 \pm 0.21) \times 10^{-4}\ s^{-1}$, and $k_{obs}(0.068) = (1.22 \pm 0.06) \times 10^{-3}\ s^{-1}$. The reaction order in CO for hydrogenolysis is $a_{CO}(II) = -1.1 \pm 0.26$.[46]

The complicated behavior observed in Figure 11 between 1.0–2.0 MPa is simply a result of the positive order $a_{CO}(I) = 1.75$ for the cluster fragmentation, together with the negative order $a_{CO}(II) = -1.1$ for hydrogenolysis. By normalizing the rates with use of $[RCORh(CO)_4]_t$, the two effects can be separated and the hydrogenolysis order can be obtained.

Temperature. The effect of temperature was studied at $x_{CO} = 0.034$ and $x_{H2} = 0.017$ with an initial concentration of 3,3-dimethylbut-1-ene of $x_{33DMB} = 0.024$. The four experiments were conducted at 293, 288, 283, and 277 K with initial concentrations of $Rh_4(CO)_{12}$ of 3.29 × 10^{-5}, 3.40 × 10^{-5}, 3.20 × 10^{-5}, and 3.31 × 10^{-5} mol fraction at 293, 288, 283, and 277 K, respectively. Temperature had a significant effect on the formation of $RCORh(CO)_4$. At 277 K, after 8 h of reaction only 20% conversion has occurred. Whereas approximately 100% conversion has occurred at 293 K in 8 h.

The logarithmic representation of the corresponding $Rh_4(CO)_{12}$ data is shown in Figure 13. At all temperatures, a first-order dependence on $Rh_4(CO)_{12}$ was obtained. The observed rate constants $k_{obs}(T)$ were $k_{obs}(293) = (8.17 \pm 0.14) \times 10^{-5}$, $k_{obs}(288) = (3.61 \pm 0.06) \times 10^{-5}$, $k_{obs}(283) = (1.97 \pm 0.09) \times 10^{-5}$ and $k_{obs}(277) = (1.21 \pm 0.03) \times 10^{-5}$. If $k_{obs}(I)$ is expressed as $k_{obs}(I) = k_0(I)[CO]^2[H_2]^1[33DMB]^0$ then the apparent activation energy is $E_a(I) = 76.9 \pm 12.0$ kJ/mol (18.4 ± 2.9 kcal/mol), and the corresponding apparent activation parameters are $\Delta H^{\ddagger}(I) = 74.4 \pm 12.0$ kJ/mol (17.8 ± 2.9) and $\Delta S^{\ddagger}(I) = -19.4 \pm 41.8$ J/mol K (−4.6 ± 10 cal/mol K).[48]

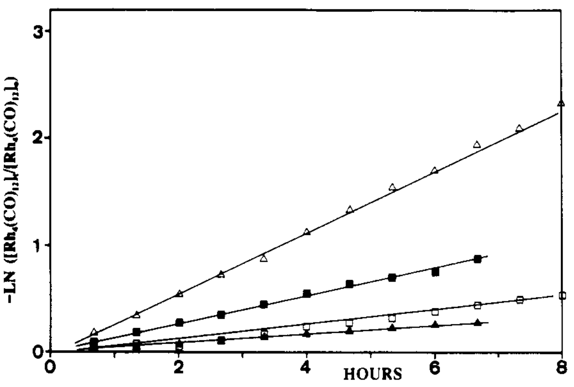

Figure 13. Effect of temperature on the rate constant k_{obs}(I) for formation of $RCORh(CO)_4$. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), 0.018 mol fraction H_2, 0.034 mol fraction CO, in *n*-hexane. Symbols are as follows: ▲, 277 K; □, 283 K; ■, 288 K; △, 293 K.

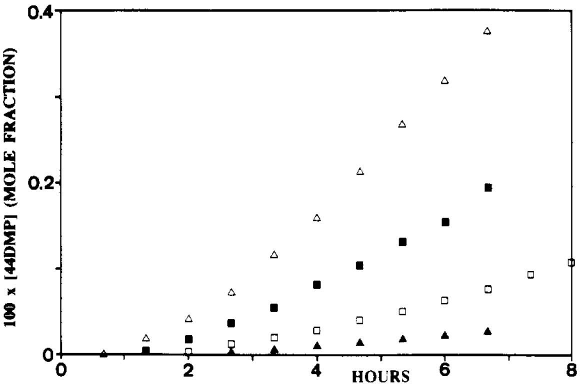

Figure 14. Effect of temperature on the formation of RCHO as a function of time. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), 0.018 mol fraction H_2, 0.034 mol fraction CO in *n*-hexane. Symbols are as follows: ▲, 277 K; □, 283 K; ■, 288 K; △, 293 K.

The calculated activation energy would have been considerably higher if the experiments had been carried out at constant partial pressures without consideration of the temperature dependence of the gas solubilities (as is often done), instead of at constant mole fraction. At constant partial pressures, the apparent activation energy would have been $E_a(I) = 90.8$ kJ/mol (21.7 kcal/mol).[49] Also, if molar units of concentration had been used instead of mole fractions, a considerably more positive entropy of activation would have been obtained $\Delta S_c^{\ddagger}(I) = 32$ J/mol K (7.4 cal/mol K).[50] These differences are artifacts introduced by taking the logarithm of a number having

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[48] The activation parameter $\Delta H^{\ddagger}$ refers to a reference state at approximately 4.0 MPa instead of the usual 0.1 MPa. The difference is accounted for by the contribution $\int \Delta V^{\ddagger}\, dP$. This integral is negligible in the present case in the limited interval 0–4.0 MPa.

[49] If $E_a(x_i)$ and $E_a(P_i)$ are defined as activation energies measured at constant mole fraction and constant partial pressures, respectively, then they are related by the following equation where ν_i are the stoichiometries (orders) for the dissolved gases, B_i are the temperature coefficients of the Henry constants, R is the gas constant, and ΔH_v is the enthalpy of vaporization of the solvent.

$$E_a(P_i) = E_a(x_i) + \sum \nu_i B_i R - \sum \nu_i \Delta H_v$$

[50] If $\Delta S_x^{\ddagger}$ and $\Delta S_c^{\ddagger}$ are the apparent entropies of activation for data taken in mole fractions and molar units of concentrations, then there is a simple relationship between these two quantities where ν_i is the stoichiometric coefficient (orders) of all reactants, R is the gas constant, ρ_m is the molar density of the solvent, and ρ^*_m is taken to be exactly 1 mol/L.

$$\Delta S_c^{\ddagger} = \Delta S_x^{\ddagger} - (1 + \sum \nu_i) R \ln (\rho_m / \rho^*_m)$$

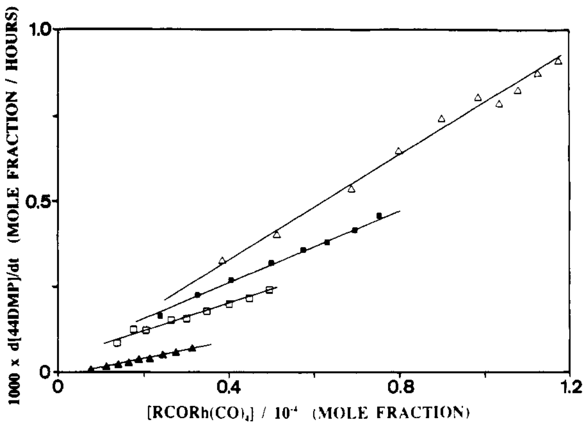

Figure 15. Effect of temperature on the rate constant k_{obs}(II) for formation of RCHO. Conditions were (3.3 ± 0.3) × 10^{-5} mol fraction $Rh_4(CO)_{12}$ (initial), 0.024 mol fraction 3,3-dimethylbut-1-ene (initial), 0.018 mol fraction H_2, 0.034 mol fraction CO in *n*-hexane. Symbols are as follows: ▲, 277 K; □, 283 K; ■ 288 K; △, 293 K.

dimensions, and by the very high reaction order for the cluster fragmentation.

As shown in Figure 14, temperature had an enormous effect on the rate of formation of 4,4-dimethylpentanal. The characteristic induction curves are present and they are considerably enhanced by the variation in temperature. The pronounced effect of temperature arises since *two* activated processes are controlling the rate of hydroformylation at initial reaction times.

Figure 15 shows a plot of the rate of formation of 4,4-dimethylpentanal versus the concentration of RCORh(CO)₄. The observed rate constants $k_{obs}(T)$ were $k_{obs}(293)$ = (2.19 ± 0.06) × 10^{-3}, $k_{obs}(288)$ = (1.63 ± 0.11) × 10^{-3}, $k_{obs}(283)$ = (1.17 ± 0.20) × 10^{-3}, and $k_{obs}(277)$ = (6.19 ± 0.46) × 10^{-4}. If k_{obs}(II) is expressed as $k_{obs}(II) = k_0(II)[CO]^{-1}[H_2]^1[33DMB]^0$ then the apparent activation energy is E_a(II) = 51.8 ± 4.0 kJ/mol (12.4 ± 0.9 kcal/mol), and the corresponding apparent activation parameters are $\Delta H^{\ddagger}$(II) = 49.3 ± 4.0 kJ/mol (11.8 ± 0.9) and $\Delta S^{\ddagger}$(II) = 121 ± 14 J/mol K (29 ± 3.4 cal/mol K).[48] If the experiments had been carried out at constant partial pressures and if the temperature dependence of the solubility of the gases had thus been neglected, then the apparent activation energy would have been E_a(II) = 61.9 kJ/mol (14.8 kcal/mol).

Discussion and Conclusions

Formation of Acylrhodium Tetracarbonyl. The kinetic results concerning the formation of acylrhodium tetracarbonyl starting from tetrarhodium dodecacarbonyl gave the nonelementary rate expression (eq 13).

$$d[RCORh(CO)_4]/dt = k_0(I)[Rh_4(CO)_{14}]^1[CO]^{1.8}[H_2]^{0.7}[33DMB]^{0.1} \quad (13a)$$

$$k_0(I) = (kT/h)\exp(-74.4\ \text{kJ}/(\text{mole}\ RT) + 19\ \text{J}/(\text{mole K}\ R)) \quad (13b)$$

The above overall rate expression (eq 13) suggests the probable bimolecular reaction of molecular hydrogen with a species $\{Rh_4(CO)_{14}\}$ as the rate-limiting step in the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ (eq 14).

$$Rh_4(CO)_{12} + 2CO \rightleftharpoons \{Rh_4(CO)_{14}\} \xrightarrow{H_2} 4RCORh(CO)_4 \quad (14)$$

Such a mechanism is suggested by the observed reaction orders and is consistent with the known mechanisms by which the fragmentation of higher nuclearity metal complexes, particularly carbonyls, to lower nuclearity species occurs.[25,26]

The 4th-order rate dependence of equation 13 is particularly important. This unusually high overall reaction order can only be rationalized in light of a preequilibrium, and in this regard, the single most important observation concerns the first-order dependence in the catalyst precursor $Rh_4(CO)_{12}$ and the second-order dependence in CO. These reaction orders suggest that a preequilibrium is established between the catalyst precursor $Rh_4(CO)_{12}$, CO, and a species with stoichiometry $\{Rh_4(CO)_{14}\}$.[51] Numerous higher nuclearity metal carbonyl clusters undergo fragmentation in the presence of carbon monoxide, and the existence of highly reactive preequilibriated intermediates of the general stoichiometry $\{M_x(CO)_{y+1,2}\}$ have been repeatedly invoked in order to rationalize the observed reaction orders.[25,26] In the present case, the intermediate $\{Rh_4(CO)_{14}\}$ would represent a cluster with at least one cleaved metal–metal bond, yielding a highly reactive open polyhedron.[52] Indeed, many metal clusters show reversible M–M cleavage.[26a,53] It then follows that the rate-determining step involves the addition of molecular hydrogen to $\{Rh_4(CO)_{14}\}$, giving rise to the observed overall 4th-order kinetics.[54] Numerous examples of hydrogen activation by metal carbonyl clusters are known.[55]

Given the above mechanistic interpretation, the measured apparent activation parameters reflect contributions from both the preequilibrium as well as the rate-determining step. However, even with the known enthalpies for Rh–Rh and Rh–CO (terminal) bond formation,[56] the interpretation of the apparent activation parameters is not straightforward. Additional complexities arise when trying to account for the influence of bridging CO's, and uncertainties in the geometry of the intermediate $\{Rh_4(CO)_{14}\}$, i.e., the number of Rh–Rh bonds broken.

Concerning the remaining elementary steps which might follow the initial activation of molecular hydrogen, no further mechanistic details can be obtained with certainty from the present kinetic results. However, given the strong evidence for the early reaction of molecular hydrogen in the reaction sequence, a hydride route rather than an unsaturated route to the initial alkene activation seems reasonable.[57] A plausible reaction scheme involves the further fragmentation to mononuclear rhodium carbonyl hydrides $\{HRh(CO)_x\}$ (x = 3,4), and then alkene insertion. Such mononuclear hydride species represent extremely unstable intermediates, which would certainly recombine to form higher nuclearity rhodium species, if alkene is not available. The small positive reaction order a_{33DMB}(I) may reflect this competition between parallel reaction pathways.

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(51) It is known, from studies of the transformation $Rh_4(CO)_{12} \rightarrow 2Rh_2(CO)_8$, that the fragmentation of $Rh_4(CO)_{12}$ is rapid ($\tau \approx$ 16 min, at 253 K and 22 MPa).[37a]

(52) Muetterties, E. L.; Burch, R. R.; Stolzenberg, A. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 89.

(53) (a) Lugan, N.; Bonnet, J. J.; Ibers, J. A. *Organometallics* **1988**, *7*, 1538. (b) Planalp, R. P.; Vahrenkamp, H. *Organometallics* **1987**, *6*, 492. (c) Schneider, J.; Minelli, M.; Huttner, G.; *J. Organomet. Chem.* **1985**, *294*, 75. (d) Schneider, J.; Huttner, G. *Chem. Ber.* **1983**, *116*, 917.

(54) Initial hydrogen activation on a lower nuclearity *preequilibrated* species, for example $Rh_2(CO)_y$ (y = 7,8) can be discounted with considerable certainty. A rate of cluster fragmentation proportional to $[Rh_4(CO)_{12}]^{1/2}$ would arise if a preequilibrium exists.

(55) (a) Farrugia, L. J.; Green, M.; Hankey, D. R.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Comm.* **1983**, 310. (b) Adams, R. D.; Wang, S. *Inorg. Chem.* **1986**, *25*, 2534. (c) Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1274.

(56) Bond enthalpies are $\Delta_f H$(Rh–Rh) = 93 kJ/mol and $\Delta_f H$(Rh–CO) = 155 kJ/mol; see: Connor, J. A. *Top. Cur. Chem.* **1977**, *71*, 71.

(57) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1982.

It is worth noting that there exists a nonnegligible increase in the Gibbs free energy of reaction $\Delta_rG^0(Rh_4(CO)_{12} \rightarrow 4RCORh(CO)_4)$ due to total pressure effects, i.e. those associated with the integral $\int \Delta_r V^\infty dP$. An approximation for the volume of reaction applicable to the fragmentation of metal carbonyl clusters was recently suggested.[58,59] From the stoichiometry of the cluster fragmentation, 8 mol of dissolved carbon monoxide and 2 mol of dissolved hydrogen are required per mole of reaction. At the temperatures and pressures used in the present study, the partial molar volumes of both carbon monoxide and hydrogen are essentially independent of pressure and are approximately 52 mL/mol and 43 mL/mol, respectively.[60] Thus, the reaction volume $\Delta_r V^\infty$ is approximately −250 mL/mol. If the integral is evaluated from ambient pressure to a typical reaction pressure of 5.0 MPa, then the increase in free energy with respect to the reference or standard condition corresponds to 8 kJ/mol (2 kcal/mol). $RCORh(CO)_4$ has a considerably smaller partial molar volume than the sum of the partial molar volumes of the reagents, hence the 8 kJ/mol represents work which is done to the system during the transformation.

It is instructive to consider the various reaction mechanisms which were circumvented due to the existence of mechanism 14 as the predominant pathway to cluster fragmentation. Indeed, numerous alternative reactions are in principle available to $Rh_4(CO)_{12}$ in this multicomponent system. First, even though $Rh_4(CO)_{12}$ undergoes various substitution reactions,[61] and even though olefin, diolefin, or arene substitutions of $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ are documented,[62] there was no evidence in the in situ spectra for such reactions either before or after the addition of H_2. This fact may be related to the relatively high liquid-phase concentration of CO, which would strongly hinder such substitution reactions. Secondly, even though both mononuclear $Rh(CO)_y$ (y = 2–4)[63] and dinuclear $Rh_2(CO)_x$ (x = 7,8)[10a,64] are known, there was no spectroscopic nor kinetic indication for such lower nuclearity metal carbonyls. Thus, even though there should be multiple reaction pathways, one mechanism, namely eq 14, is responsible for the development of the active system.[65]

Hydrogenolysis of Acylrhodium Tetracarbonyl. The activity of the present rhodium-catalyzed hydroformylation system was shown to be proportional to the concentration of the mononuclear intermediate $RCORh(CO)_4$ under all reaction conditions studied. It proved convenient to measure the activity in terms of a pseudo-first-order rate constant k_{obs}(II) where the following reaction orders and apparent activation parameters were found (eq 15).[66]

$$d[RCHO]/dt = k_0(II)[RCORh(CO)_4]^1[CO]^{-1.1}[H_2]^1[33DMB]^{0.1} \quad (15a)$$

$$k_0(II) = (kT/h)\exp(-49.3\ kJ/(mole\ RT) - 121\ J/(mole\ K\ R)) \quad (15b)$$

The prior dissociation of a carbonyl ligand before the activation of molecular hydrogen is clearly indicated by the term $[RCORh(CO)_4][CO]^{-1.1}$, and by the positive entropy of activation. Thus, there is a preequilibrium between the relatively stable saturated and observable intermediate $RCORh(CO)_4$, and a coordinately unsaturated and highly reactive species of stoichiometry $\{RCORh(CO)_3\}$ at which the actual activation of molecular hydrogen occurs (eq 2). The nonzero and slightly positive reaction order $a_{33DMB}(II) = 0.1 \pm 0.05$ may again reflect the role of 3,3-dimethylbut-1-ene as a scavenger for the highly reactive rhodium carbonyl hydrides, thus hindering the reverse reaction of eq 2, and/or recombination of rhodium carbonyl hydrides.

The measured apparent activation parameters $\Delta H^\ddagger$ = 49.3 ± 4.0 kJ/mol and $\Delta S^\ddagger$ = 121 ± 14 J/mol K contain a contribution from the preequilibrium between $RCORh(CO)_4$, CO, and $\{RCORh(CO)_3\}$. If 24 kJ/mol is assumed to be the smallest possible enthalpy difference between a saturated $18e^-$ $XRh(CO)_4$, CO, and an unsaturated $16e^-$ $XRh(CO)_3$,[67] then the enthalpy of activation for the oxidative addition of molecular hydrogen at $\{RCORh(CO)_3\}$ is $\Delta H^\ddagger \leq 25$ kJ/mol. Considering the apolar solvent used, the low value of $\Delta H^\ddagger$ probably indicates the simple addition of molecular hydrogen at rhodium through a three-center transition state instead of across the RCO–Rh bond as a four-center transition state.[68] The present entropy of activation can be compared to $\Delta S^\ddagger$ = 62 J/mol K for the hydrogenolysis of $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ in toluene where the prior dissociation of PPh_3 is required.[33]

In principle, the bimolecular reaction of $\{RCORh(CO)_3\}$ with molecular hydrogen is not the only mechanism available for the hydrogenolysis of $RCORh(CO)_4$. In addition, there is the possibility that some aldehyde formation occurs via a bimolecular elimination reaction, similar

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[58] The volume of reaction for the fragmentation of metal carbonyl clusters under CO to lower nuclearity species can be approximated by the following summation where ϕ is an empirically determined constant ($\phi \approx 0.5$), ν_i are the stoichiometries for the i-th gaseous component, and v_i are the corresponding partial molar volumes.[59]

$$\Delta_r V^\infty = \phi \sum \nu_i v_i$$

To a first approximation, the difference in the Gibbs free energy of reaction for the fragmentation of a metal carbonyl cluster is then given by

$$\Delta_r G(T,P_{ref}) - \Delta_r G(T,P) = (0.5 \sum \nu_i v_i) \int dP$$

[59] Garland, M.; Horvath, I. T.; Bor, G.; Pino, P. *Organometallics* **1991**, *10*, 559.

[60] (a) Connolly, J. F.; Kandalic, G. A. *J. Chem. Thermodyn.* **1984**, *16*, 1129. (b) Walkley, J.; Jenkins, W. I. *Trans Faraday Soc.* **1968**, *64*, 19. (c) Handa, Y. P.; Benson, G. C. *Fluid Phase Equilib.* **1982**, *8*, 161. (d) At 344 K in *n*-hexane, the partial molar volume of molecular hydrogen is 64 mL/mol, see: Orentlicher, M.; Prausnitz, J. M. *Chem. Eng. Sci.* **1964**, *19*, 775.

[61] (a) Booth, B. L.; Else, M. J.; Fields, R.; Hazeldine, R. N. *J. Organomet. Chem.* **1971**, *27*, 119. (b) Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380. (c) Sartorelli, U.; Canziani, F.; Martinengo, S.; Chini, P. *Proc. Int. Conf. Coord. Chem.* **1970**, *12*, 144. (d) Whyman, R. *J. Chem. Soc., Dalton Trans.* **1972**, 1375. (e) Chini, P.; Heaton, B. T. *Top. Cur. Chem.* **1977**, *71*, 1. (f) Kennedy, J. R.; Basolo, F.; Trogler, W. C. *Inorg. Chim. Acta* **1988**, *146*, 75. (g) Brodie, N. M. J.; Poë, A. J. *J. Organomet. Chem.* **1990**, *386*, 531.

[62] (a) Stuntz, G. F.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 9. (b) Ros, R.; Scrivanti, A.; Roulet, R. *J. Organomet. Chem.* **1986**, *303*, 273. (c) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; *J. Chem. Soc., Chem. Comm.* 1971, 36.

[63] (a) Ozin, G. A.; Hanlan, A. J. L. *Inorg. Chem.* **1979**, *18*, 2091. (b) Hanlan, L. A.; Ozin, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6324.

[64] Chenier, J. H. B.; Histed, M.; Howard, J. A.; Joly, H. A.; Morris, H.; Mile, B. *Inorg. Chem.* **1989**, *28*, 4114.

[65] It has been suggested that the formation of $HRh(CO)_4$ may occur via the activation of molecular hydrogen on dinuclear rhodium carbonyl species. Such a mechanism can not be discounted at reaction conditions which are significantly removed from the present case. Vidal, J. L.; Schoening, R. C.; Walker, W. E. *ACS Symp. Ser.* **1980**, *155*, 61.

[66] At initial reaction times, a significantly higher apparent activation energy would have been measured if induction had not been decoupled from the overall kinetics. This may explain to some extent the usually higher activation energies obtained from overall kinetic measurements for the hydroformylation reaction, for example E_a = 27 kcal/mol,[1] and E_a = 38 kcal/mol.[70]

[67] An enthalpy difference of $\Delta_r H^0$ = 24 kJ/mol has been measured between the coordinately unsaturated species $CoRh(CO)_7$, CO, and the coordinatively saturated species $CoRh(CO)_8$.[59]

[68] James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford 1982.

to that found for the unmodified cobalt system, i.e. $HCo(CO)_4 + RCOCo(CO)_4 \rightarrow RCHO + Co_2(CO)_8$ under noncatalytic reaction conditions.[69] However, all the experimental data presented in this study indicates that the rate of hydroformylation is *only* first order in the concentration of rhodium in the active system. No higher order dependence is suggested. Therefore, we conclude that the contribution of a bimolecular elimination to the total net rate of aldehyde formation is probably negligible at the reaction conditions used in this study. Of course, this conclusion does not exclude the *existence* per se of such a mechanism.

$$HRh(CO)_x + RCORh(CO)_y \rightarrow RCHO + Rh_2(CO)_{x+y} \quad (16)$$

For completeness, it should be noted that entirely different interpretations and conclusions have been obtained in at least two previous studies of the unmodified rhodium catalyzed hydroformylation reaction, and in both, higher nuclearity species were believed to be responsible for the steady-state kinetics. In a rather early study, Yamaguchi concluded that the hydroformylation reaction occurred on a dinuclear species $Rh_2(CO)_7$.[70] In a much more recent study, the hydroformylation of cyclohexene at 125 °C was attributed to cluster catalysis on an open $\{H_2Rh_4(CO)_{12}\}$ species.[71] However, these higher nuclearity interpretations explicitly assume that both hydrogen atoms which are incorporated into the product aldehyde originate from the same molecule of dissolved hydrogen. D_2/H_2 experiments have conclusively shown that the hydrogen atoms which are incorporated into the product aldehyde originate from two different molecules of hydrogen.[72]

Carbon Monoxide Insertion and Definition of TOF. There is a fundamental question concerning the nature of $RCORh(CO)_4$ which needs to be addressed in light of the present experiments. It has been proposed, that the formation of Group VIIIB (Co, Rh, Ir) acylmetal tetracarbonyls from alkylmetals carbonyls may proceed through either of two mechanisms. These mechanisms are (A) a two-step CO insertion starting from the corresponding alkylmetal tetracarbonyl (eq 17) and consistent with Figure 1 and (B) a concerted CO insertion mechanism (eq 18).[73] Of course, the general problem of CO insertion into metal–alkyl bonds is one of the most investigated mechanistic steps in all organometallic chemistry.[74]

$$RRh(CO)_4 \rightleftharpoons \{RCORh(CO)_3\} \xrightleftharpoons{CO} RCORh(CO)_4 \quad (17)$$

$$RRh(CO)_4 \xrightleftharpoons{CO} RCORh(CO)_4 \quad (18)$$

The existence of mechanism A or B as the primary mode of CO insertion under *catalytic conditions* is important. If mechanism A is operating, then the species $RCORh(CO)_4$ lies outside the catalytic cycle as a reservoir (as shown in Figure 1), whereas if mechanism B is important, then $RCORh(CO)_4$ is in fact an intermediate on the cycle. Further, the two mechanisms lead to two entirely different mass balances for the total concentration of intermediates on the active catalytic cycle but no difference for the mass balance on the active system. Discussion of the general reservoir problem for catalytic systems can be found in the literature.[75]

The present kinetic results provide no new and significant insight into the CO insertion step for unmodified rhodium catalyzed hydroformylation. The present experimental results cannot differentiate between the two possible cases. We note however, that from a chemical viewpoint, a concerted CO insertion step might be preferred in the noncoordinating solvent *n*-hexane. Indeed, concerted mechanisms have much in common with solvation phenomena.[76] Also, ab initio calculations, at least in the case of manganese, show a decided thermodynamic advantage for a concerted mechanism for CO insertion as opposed to a two-step mechanism.[77]

As stated in conjunction with eq 12, the rate constant $k_{obs}(II)$ can be set equal to a turn over frequency (TOF) based on a mass balance for the *active system*. Such a definition avoids the uncertainty concerning the mode of CO insertion, or in other words, the exact position of $RCORh(CO)_4$ in the reaction scheme. Indeed, the concentration of $RCORh(CO)_4$ represents (to a very good approximation) a measure of the total concentration of mononuclear complexes in the active system. This includes both the mononuclear intermediates in the active cycle as well as complexes which may be in equilibrium exchange with the cycle. Hence, the above interpretation of $k_{obs}(II)$ represents a conservative definition for the turnover frequency of the unmodified rhodium catalyzed hydroformylation reaction. Under the reaction conditions used in this study, the turn over frequencies of the unmodified rhodium catalyzed hydroformylation reaction are very low ($0.04/\text{min} \le \text{TOF} \le 0.27/\text{min}$).

$$k_{obs}(II) \equiv \text{TOF} \quad (19)$$

Activity. If the activity of the entire system is expressed by the rate 33DMB → 44DMP in mole fraction per second, then the activity of the present experiments can be partitioned into the time-dependent term $[RCORh(CO)_4]_t$ and the time-independent term TOF where $[RCORh(CO)_4]_t = f(x_1...x_n,T,t)$ and $\text{TOF} = f(x_1...x_n,T)$. It is readily seen that the macroscopic activity of the system is a complicated function of the parameters x_{H2}, x_{CO}, and T for all initial reaction times. Equation 20, and its appropriate derivatives with respect to x_{H2}, x_{CO}, and T, provide a direct explanation of the complicated experimental results shown in Figures 7, 11, and 14.

$$\text{activity} = [RCORh(CO)_4]_t\text{TOF} \quad (20)$$

The system approaches its maximum activity in the limit as $[RCORh(CO)_4]_t$ approaches $[RCORh(CO)_4]_{max} = 4[Rh_4(CO)_{12}]_0$. To a good approximation, the time-dependent concentration of $RCORh(CO)_4$ for the present experiments is given by eq 21. The eigenvalue $\lambda = k_0$-

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Organometallics **1991**, *10*, 1704–1709

$(I)[CO]^{1.8}[H_2]^{0.7}[33DMB]_0^{0.1}$ completely controls the development of the active hydroformylation system.

$$[RCORh(CO)_4]_t = 4[Rh_4(CO)_{12}]_0 \times (1 - \exp(-k_0(I)[CO]^{1.8}[H_2]^{0.7}[33DMB]_0^{0.1}t)) \quad (21)$$

In conclusion, this study has presented a systematic approach for decoupling induction and steady-state kinetics for the unmodified rhodium catalyzed hydroformylation reaction. The present analysis illustrates the usefulness of treating, as far as possible, the precatalytic and catalytic reaction sequences individually. Without proving that the transformation of a precursor has occurred, or even to what degree it has occurred, it is difficult to accurately speak of the activation energies and the reaction orders associated with the steady-state kinetics of a catalytic cycle. Even though only induction and steady-state kinetics appear in this particular homogeneously catalyzed reaction, it is possible to broaden the context, and to include deactivation as well. The inclusion of deactivation kinetics into the present approach is straightforward. Such a case, where induction, steady-state kinetics, and deactivation all appear and can be decoupled from the overall dynamics, has already been treated.[22,23]

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Supplementary Material Available: A typical in situ infrared spectrum of $Rh_4(CO)_{12}$, CO, and 3,3-dimethylbut-1-ene in *n*-hexane prior to the addition of hydrogen, a plot of $k_{obs}(I)$ as a function of the 3,3-dimethylbut-1-ene concentration, a plot of $RCORh(CO)_4$ as a function of the liquid phase concentration of hydrogen and as a function of time, and a plot of $RCORh(CO)_4$ as a function of temperature and as a function of time (3 pages). Ordering information is given on any current masthead page.

Unusual η^6-Toluene Coordination to an Alkali Metal. X-ray Crystal Structure of $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(\eta^6\text{-}C_7H_8)_2$ and the Solubilization of Unsolvated Alkali-Metal Halides in Hydrocarbon Media

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Reaction of $Lu\{CH(SiMe_3)_2\}_3$ (**1**) with KCl in ether, or reaction of $LuCl_3$ with $KCH(SiMe_3)_2$ (3 equiv) in ether, affords $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(ether)$ (**2**). Coordinated ether is readily removed from **2** under vacuum to afford $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K$ (**3**), which contains coordinated KCl that is not stabilized by a donor ligand. Reaction of **1** with KBr yields $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Br)K(ether)$ (**4**), which can be converted to $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Br)K(C_7H_8)$ (**5**). Dissolution of **3** in toluene affords $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)_2$ (**6**). Stepwise removal of coordinated toluene from **6** can be achieved, first to give the mono(toluene) adduct $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(C_7H_8)$ (**7**), and finally to **3**. Compound **6** crystallizes in space group $P\bar{1}$ (No. 2), with $a = 12.0060$ (12) Å, $b = 13.9624$ (14) Å, $c = 16.5370$ (42) Å, $\alpha = 105.44$ (4)°, $\beta = 99.77$ (7)°, $\gamma = 106.27$ (10)°, $V = 2474$ Å^3, and $Z = 2$. The current $R = 0.051$ and $R_w = 0.061$ for 6445 independent reflections with $I > 2.5\sigma(I)$. **6** shows unusual η^6 coordination of both toluenes to potassium. In contrast, neither $La\{CH(SiMe_3)_2\}_3$ nor $Lu(C_5Me_5)_2CH(SiMe_3)_2$ reacts with KCl in ether.

Introduction

Salt coordination is a ubiquitous, if undesirable, phenomenon in organolanthanide chemistry,[1] arising as a consequence of general synthetic procedures involving alkylation. Removal of this coordinated salt often necessitates an ingenious sequence of reactions.[2] Coordination of an alkali-metal halide to an electron-deficient lanthanide is invariably associated with its stabilization by a donor ligand such as ether, THF, or a chelating amine. In addition, the solubilization of alkali-metal salts in hydrocarbon media by in situ methods has been the subject of considerable recent attention,[3] direct dissolution of $(MX)_\infty$ with nonmacrocyclic ligands not always being successful, due to difficulties associated with the aggre-

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