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The competitive and non-competitive hydroformylation of conjugated dienes starting with tetrarhodium dodecacarbonyl. An in-situ high-pressure infrared spectroscopic study☆

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Abstract

It is well known that the liquid-phase homogeneous unmodified rhodium catalysed hydroformylation of alkenes is poisoned by the presence of trace quantities of conjugated dienes. Nevertheless, some hydroformylation of conjugated dienes is possible with unmodified rhodium, and this reaction is in general slower than alkene hydroformylations at comparable reaction conditions. In the present contribution, we examined (A) the catalytic behaviour of alkenes in the presence of trace conjugated diene impurities and (B) the catalytic behaviour of a variety of dienes using $Rh_4(CO)_{12}$ in *n*-hexane solvent at 293 K under 1.0–4.0 MPa CO and 0.5–2.0 MPa H_2. The analytic method was in-situ high-pressure infrared spectroscopy. It was observed that (I) in the hydroformylation of poisoned alkenes, most of the rhodium reacts with the trace quantity of conjugated dienes and not the alkenes in this competitive situation and (II) the metal carbonyl spectra of the hydroformylation of a variety of dienes are very similar. The primary absorbance maxima observed in the hydroformylations of conjugated dienes occur at circa 2109, 2091, 2087, 2064, 2049, 2037, 2030, 2020, 2012, 1999, and 1990 cm^{-1}. Given the known chemistry of $Rh_4(CO)_{12}$ under syngas, and the very well documented chemistry of $Rh_4(CO)_{12}$ under alkene hydroformylation conditions, the lack of bridging carbonyls in the present experiments strongly suggested that the new infrared vibrations are due to mononuclear rhodium species. Preliminary analysis suggests the presence of at least three new species. In particular, the formation of observable η^3 allyl rhodium tricarbonyl species, σ allyl rhodium tetracarbonyl species and even acyl rhodium tetracarbonyl species $RCORh(CO)_4$ (R = alkenyl and/or formylalkyl) seems probable. Characteristic wavenumbers of 2108, 2064, 2037, 2020 and 1700 cm^{-1} are tentatively assigned to the latter. The reduced hydroformylation activity in the competitive hydroformylation of alkenes arises due to the much higher affinity of rhodium complexes for conjugated dienes than for alkenes under otherwise similar reaction conditions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tetrarhodium dodecacarbonyl; Hydroformylation; Dienes; Deactivation; Rhodium complexes

1. Introduction

The unmodified rhodium catalysed hydroformylation reaction has been known for almost 50 years [1], and a few early reviews contain much of the knowledge concerning reactivity and substrate dependences [2]. In addition, a host of early kinetic work on alkene hydroformylation [3], the chemistry associated with the transformation of rhodium carbonyls [4], and in-situ spectroscopic/kinetic studies of alkene hydroformylations and the identification of $RCORh(CO)_4$ [5], have added considerably to our knowledge of this reaction. However, a few large gaps in the understanding of the hydroformylation reaction still exist. For example, it is widely known that the unmodified rhodium catalysed hydroformylation is very sensitive to a number of impurities including trace quantities of alkynes and dienes [6]. Recently, in-situ spectroscopic studies showed that in the presence of trace alkynes, $Rh_4(CO)_{12}$ is quantitatively transformed to dinuclear alkyne rhodium car-

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☆ Primary experimental research was performed at ETH-Zurich 1992–1995. Analysis was performed at the National University of Singapore 1998.

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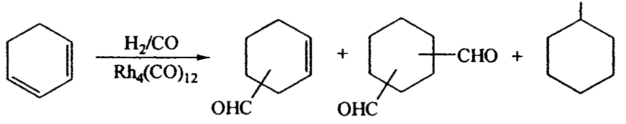
bonyl complexes under hydroformylation conditions, thereby preventing the availability of rhodium for alkene hydroformylation [7]. In the present contribution, we extend our investigation to conjugated dienes.

The homogeneous hydroformylations of conjugated dienes were first extensively investigated using soluble cobalt complexes by Natta [8] and Adkins [9]. Later stoichiometric studies showed that cobalt carbonyl hydride readily attacked conjugated dienes, leading to the formation of η^3 allyl cobalt tricarbonyl species as well as σ allyl cobalt tetracarbonyl species under stoichiometric conditions [10–13]. In-situ IR spectroscopic studies of 1,3-butadiene were undertaken by Mirbach and the corresponding $(\eta^3\text{-}C_4H_7)Co(CO)_3$ was observed [14]. Other direct in-situ spectroscopic support for η^3 allyl cobalt species comes from King and Tanaka who prepared $(\eta^3\text{-}C_3H_5)Co(CO)_3$ and observed its interconversion to $CH_2{=}CH{-}CH_2{-}Co(CO)_4$ [15]. Together, these studies lend strong support for the presence of both η^3 allyl cobalt species as well as σ allyl cobalt species under catalytic conditions [16]. It can be noted that vibrational and NMR studies have been conducted on $(\eta^3\text{-}C_4H_7)Co(CO)_3$ [17,18].

The cobalt catalysed hydroformylation of conjugated dienes normally leads to the formation of saturated mono-aldehydes and not the twice hydroformylated products [2b,19]. A variety of conjugated dienes have been hydroformylated, including 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, 3-methyl-1,3-pentadiene, cyclopentadiene, vinylcyclohexene, and 1,5-cyclooctadiene [9,20,21].

In the case of rhodium catalysed hydroformylation of dienes, numerous substrates have been studied with [22] and without phosphine ligands present [23]. The unmodified rhodium catalysed reaction exhibits the same primary characteristics as the cobalt catalysed hydroformylation of dienes, namely, a strong tendency for the production of the saturated monoaldehydes and not the twice hydroformylated products [2b]. However, the addition of phosphine ligands substantially changes the reaction characteristics and leads to twice hydroformylated products.

The problem of organic product selectivity in the rhodium catalysed hydroformylation of conjugated dienes is illustrated by Eq. (1) where 1,3-cyclohexadiene is the substrate.



(1)

In the present contribution we investigate the hydroformylation activity of a variety of conjugated dienes in the presence of $Rh_4(CO)_{12}$ in *n*-hexane as solvent at 293–298 K at circa 1.0–4.0 MPa CO and 0.5–2.0 MPa H_2: in both a non-competitive situation and competitive situation with alkenes. Both non-cyclic dienes such as 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene and cyclic dienes such as 1,3-cyclohexadiene and 1,3-cyclooctadiene were used. The primary objective of the study was to obtain in-situ IR spectroscopic evidence for the existence of new rhodium complex(es) under hydroformylation conditions when dienes are present. The second objective was to understand better the role of dienes in the poisoning of alkene hydroformylations. The present contribution attempts to expand on the very limited body of knowledge concerning the homogeneous catalytic hydroformylation of dienes in the presence of unmodified rhodium carbonyls.

2. Experimental

2.1. General information

All solution preparations were carried out under argon (99.999% Pan Gas AG, Luzern, Switzerland or 99.999% Saxol Singapore) using standard Schlenk techniques [24]. The argon was further purified prior to use by passage through a column containing 100 g reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieve to adsorb trace oxygen and water respectively. All reactions were carried out under carbon monoxide (99.997% Messner Griesheim GmbH, Germany) and hydrogen (99.999% Pan Gas AG, Luzern, Switzerland, or 99.999% Saxol, Singapore) after further purification through de-oxy and zeolite columns.

The precious metal complex $Rh_4(CO)_{12}$, with stated purity of 98% min, was obtained from Strem Chemicals SA (Bischheim, France or Newbury Port, MA) and was used without further purification, although trace quantities of the high nuclearity cluster $Rh_6(CO)_{16}$ are virtually always present. The complex $Rh_4(CO)_{12}$ is known to be oxygen, water and light sensitive [25]. The *n*-hexane solvent (stated purity $> 99.6\%$, Fluka AG) was refluxed over sodium potassium alloy under argon. Weights were measured with a precision of ± 0.1 mg. Volumes were measured with a precision of ± 0.045 ml. Further microanalytic techniques were not employed [26]. All conjugated dienes used in this study were of the highest quality commercially obtainable, usually 99.0 + % (Fluka AG Switzerland, Merck Germany) and the *cis* oct-4-ene was obtained from ChemSampCo Ohio. Concerning further purification, the conjugated dienes were simply degassed before use and the *cis* oct-4-ene was dried over CaH_2 under nitrogen.

2.2. Equipment

In-situ spectroscopic studies were performed in a 1.5 l stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) which was connected to a high-pressure IR cell. The autoclave ($P_{\max} = 22.5$ MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie, PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (model DMK 30, Orlita AG, Geissen, Germany), with a maximum rating of 32.5 MPa and a 3 l h^{-1} 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 inch (SS316) high-pressure tubing (Autoclave Engineers). The entire system, consisting of autoclave, pump, transfer lines and IR cell, was cooled using a Lauda RX20 cryostat or a Polyscience cryostat model 9505 and could be maintained isothermal ($\Delta T \approx$ 0.5°C) at 298–313°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 inch (SS316) high-pressure tubing (Autoclave Engineers) and 1.0, 5.0, 10.0 piezocrystals were used for pressure measurements (Keller AG Winterthur, Switzerland). The entire system was gas tight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure IR 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 [27] is a variation on a design due to Noack [28], and differs in some respects from other high-pressure IR cells described in the literature (for a review, see Whyman [29]). The high-pressure cell was situated in a Perkin–Elmer 983 IR spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A schematic diagram of the experimental setup can be found in ref. [11]. In the competitive experiments with *cis* oct-4-ene poisoned by dienes, a Perkin–Elmer system 2000 FTIR spectrometer was used.

2.3. In-situ spectroscopic studies

All experiments were performed in a similar manner. First, single beam background spectra of the IR sample chamber were recorded. Then, either (A) 10 ml of *cis* oct-4-ene or (B) 1–10 ml diene, was dissolved in 150 ml *n*-hexane and this solution was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, IR spectra of the alkene–diene solution in the high-pressure cell were recorded. The total system pressure was raised to 1.0–4.0 MPa CO, and the stirrer and high-pressure membrane pump were started. After vapor–liquid equilibration, IR spectra of the alkene–diene–*n*-hexane–CO solution in the high-pressure cell were recorded. A solution of 100 mg $Rh_4(CO)_{12}$ dissolved in 100 ml *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO and then added to the autoclave. IR spectra of the alkene–diene–*n*-hexane–CO–$Rh_4(CO)_{12}$ solution in the high pressure cell were recorded. 0.5–2.0 MPa hydrogen was then added. Spectra were recorded at 30 min intervals in the range 1600–2200 cm^{-1}. A considerable number of spectral subtractions were performed on each reaction spectrum in order to subtract the absorbance of the *n*-hexane solvent, dissolved CO, alkene, diene, and the absorbance of the $Rh_4(CO)_{12}$.

At 2.0 MPa partial pressures, the solubility of CO under these reaction conditions was approximately 0.033 mol fraction, and the solubility of H_2 was approximately 0.018 mol fraction [9]. Consequently, a typical experiment used circa 1.51 mol *n*-hexane, 0.05 mol CO and 0.03 mol H_2. Since the amounts of $Rh_4(CO)_{12}$ used in the experiments were circa 100 mg, and since the concentration of alkenes/dienes was low, the corresponding in-situ measured initial concentrations of $Rh_4(CO)_{12}$ in the experiments were circa 8×10^{-5} mol fraction.

3. Results

3.1. Various dienes

In this comparative study, 1,3-cyclooctadiene, 1,3-cyclohexadiene, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene were used. These dienes were used under a wide range of partial pressures in order to identify reaction conditions leading to the highest conversion of $Rh_4(CO)_{12}$, and/or the most interesting metal carbonyl spectra. After a few hours of reaction time, and in most cases, significant conversions of $Rh_4(CO)_{12}$ were achieved.

Fig. 1 shows representative spectra for the hydroformylation of the above mentioned substrates. First, it can be noted that the characteristic wavenumbers for the metal carbonyl spectra are rather similar, although the relative magnitudes are not. Secondly, the appearance of aldehyde is clearly shown at circa 1730 cm^{-1} in the spectra of 1,3-cyclooctadiene, 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene. Thirdly, only 2-methyl-1,3-butadiene shows little if any hydroformylation product. (The reason for this anomalous lack of activity is not clear.) However, close inspection shows a small vibration at circa 1703 cm^{-1} which is probably due to the presence of a mononuclear rhodium acyl complex

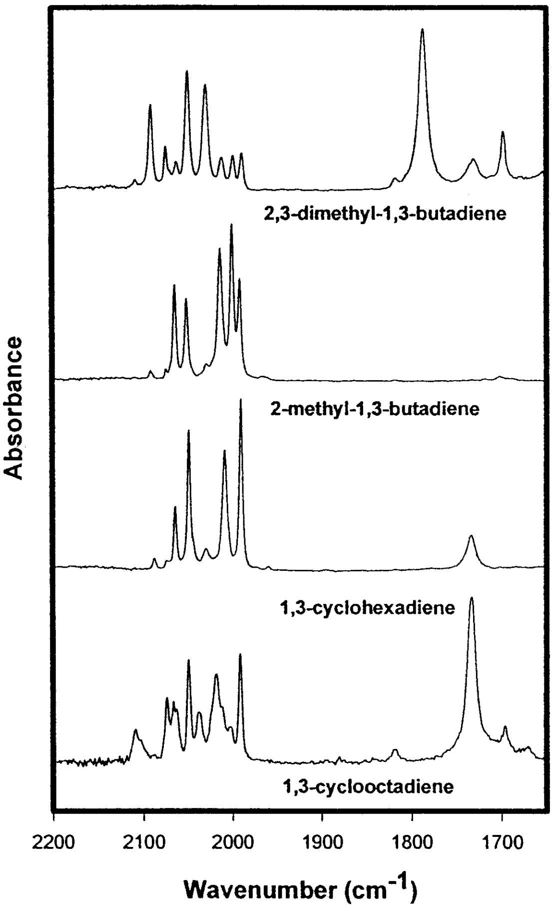


Fig. 1. In-situ high-pressure IR spectra of the reaction of $Rh_4(CO)_{12}$ under syngas at 293 K and in the presence of conjugated dienes. Total reaction time is a few hours. Hexane and dissolved CO subtraction has been performed.

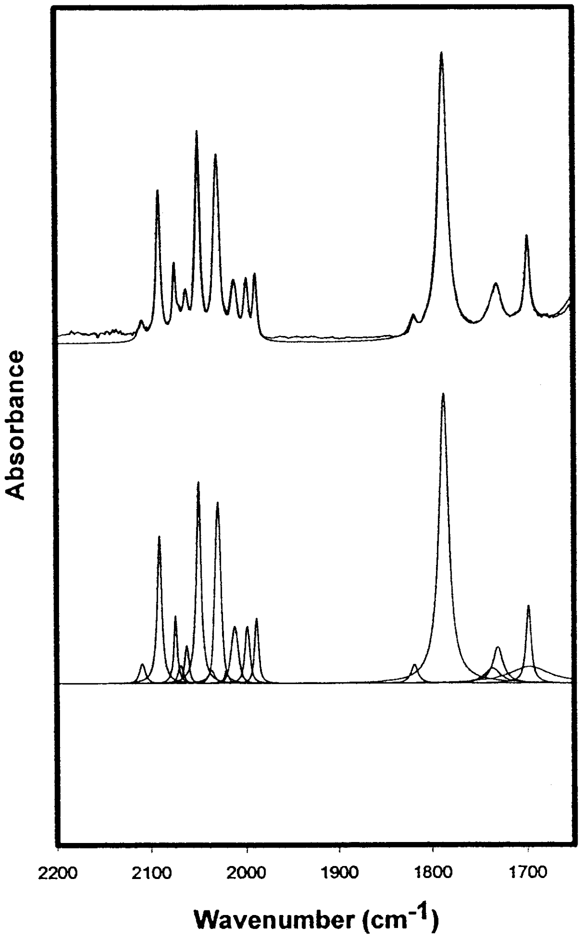


Fig. 2. Deconvolution of 2,3-dimethyl-1,3-butadiene spectrum in the metal–carbonyl interval. Top curves represent original spectrum and best fit. Bottom curve represents the deconvolution.

since the wavenumber is consistent with our previous observations of the acyl moiety in $RCORh(CO)_4$ [5].

Table 1 allows a closer inspection of the metal carbonyl region. As seen, there is considerable correspondence in the wavenumber maxima.

Other conjugated dienes were used as well at 293 K. These were 2,3-diphenyl-1,3-butadiene, and 1,4-diphenyl-1,3-butadiene. In these experiments, significant conversion of $Rh_4(CO)_{12}$ did not take place during the experiments, and new spectral characteristics did not appear.

3.2. Details of 2,3-dimethyl-1,3-butadiene

Deconvolution of the hydroformylation spectrum of 2,3-dimethyl-1,3-butadiene was performed. This is shown in Fig. 2.

Table 1
The wavenumbers of the conjugated diene complexes[a]

Conjugated diene	Wave number (cm^{-1})							
2,3-Dimethyl-1,3-butadiene	**2108.8**		2090.8		*2073.9*	2068.4	**2062.1**	2049.7
2-Methyl-1,3-butadiene			2091.1		*2074.5*		**2064.6**	2051.1
1,3-Cyclohexadiene				2087.9	*2074.4*		**2064.6**	2049.1
1,3-Cyclooctadiene	**2108.9**	2103.0	2091.1	2087.5	*2074.4*	2066.7	**2063.7**	2049.4
2,3-Dimethyl-1,3-butadiene	**2036.3**	2029.2	**2020.4**	*2011.6*		*1998.6*	1988.4	
2-Methyl-1,3-butadiene		2029.2	**2020.5**	*2012.9*		*1999.7*	1991.0	1965.3
1,3-Cyclohexadiene		2030.0			2008.3		1989.9	1960.2
1,3-Cyclooctadiene	**2038.1**		**2018.5**	*2012.5*		*2003.6*	1991.7	

[a] Different fonts represent groups of bands which appear to be related to one and the same species.

In the high wavenumber region, more band maxima can be identified. In particular, these are 2108.8, 2090.8, 2073.9, 2068.4, 2062.1, 2049.7, 2036.3, 2029.2, 2020.4, 2011.6, 1998.6 and 1988.4 cm^{-1}. From our previous in-situ spectroscopic studies, it is possible immediately to assign the band at 2073.9 cm^{-1} to the ubiquitous $Rh_6(CO)_{16}$. Furthermore, the bands at 2108.8, 2062.1, 2036.3 and 2020.4 cm^{-1} have the correct positions and intensities for mononuclear acyl rhodium tetracarbonyls.

In the low wavenumber region, the primary spectral characteristics appear at 1818.4, 1787.2, 1736.4, 1730.5, 1698.3, 1697.0 and a wide band at 1645.3 cm^{-1}. Again, the band at 1818.4 cm^{-1} is clearly due to $Rh_6(CO)_{16}$, and the band at 1787.2 cm^{-1} is the unsubtracted diene. This leaves four or five new bands which must be explained. The bands at 1736.4 and 1730.5 cm^{-1} suggest two spectroscopically distinct aldehydes, and the bands at 1698.3 and 1697.0 cm^{-1} suggest two spectroscopically distinct acyl groups. If a conjugated C=C/C=O system arises as an intermediate or final product, this would lead to a broad C=C vibration, and this is consistent with the broad feature at 1645.3 cm^{-1}.

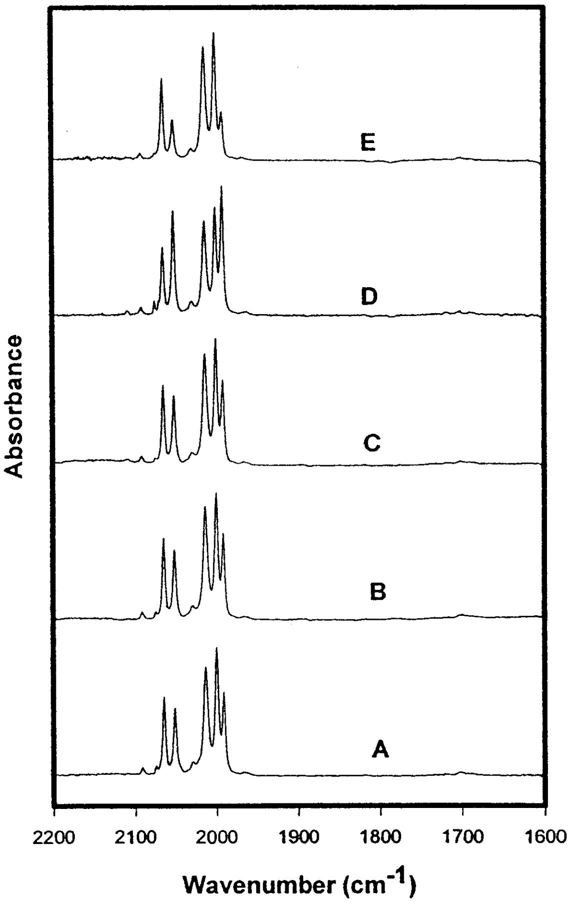


Fig. 3. The reaction of $Rh_4(CO)_{12}$ with 2-methyl-1,3-butadiene under varying CO and H_2 partial pressures. A, 2.0 MPa CO, 0.5 MPa H_2. B, 2.0 MPa CO, 1.0 MPa H_2. C, 2.0 MPa CO, 2.0 MPa H_2. D, 1.0 MPa CO, 1.0 MPa H_2. E, 4.0 MPa CO, 1.0 MPa H_2.

3.3. Different reaction conditions for 2-methyl-1,3-butadiene

The reaction of 2-methyl-1,3-butadiene with $Rh_4(CO)_{12}$ was studied at five different partial pressures of CO and H_2. One spectrum from each reaction condition is shown in Fig. 3. The characteristic wavenumbers can be found in Table 1.

Inspection of the spectra indicates that the CO partial pressure plays a significant role, whereas the partial pressure of H_2 hardly affects the spectral characteristics (and distribution of species). In particular, it seems that the bands at 2051, 2029 and 1991 cm^{-1} move together with approximate intensities of 0.8:0.1:1, and increase with decreasing CO partial pressure. This suggests that these bands probably arise from a rhodium tricarbonyl species. In addition there are three bands at 2000, 2013 and 2065 cm^{-1} which move together with approximate intensities of 1:0.9:0.7.

The very weak band seen at 1965 cm^{-1} in all spectra is circa 25 cm^{-1} lower than the prominent vibration at 1991 cm^{-1}. This very weak signal is most likely due to the isotopomers, i.e. the 1.1% natural abundance of ^{13}CO [30].

Finally, in the interest of completeness, it can be noted that the spectra of the hydroformylation experiments with the other conjugated dienes also showed strong CO and H_2 dependences, i.e. the distribution of intermediates was strongly effected.

3.4. Deconvolution of the metal–carbonyl region

The deconvolution of the metal–carbonyl interval (from the hydroformylation of 2-methyl-1,3-butadiene) is shown in Fig. 4. The characteristic vibrations after deconvolution are 2091.1, 2074.5, 2064.6, 2051.1, 2029.2, 2020.5, 2012.9, 2007.1, 1999.7, 1991.0, 1965.3 cm^{-1}. The band at 2020.5 cm^{-1} was obscured before deconvolution. The band at 2074.5 cm^{-1} can be assigned to $Rh_6(CO)_{16}$.

3.5. Competitive hydroformylation of cis oct-4-ene

Hydroformylation of *cis* oct-4-ene was performed at 4.0 MPa CO and 2.0 MPa H_2. The in-situ high-pressure IR spectra in the region 2200–1600 cm^{-1} were not very similar to other alkene hydroformylations performed in this laboratory [5]. Instead of observing only four new metal–carbonyl vibrations at approximately 2108, 2061, 2037 and 2019 cm^{-1} for a symmetric internal linear alkene [5h,31], about nine new vibrations appeared. These new vibrations occurred at 2107.3, 2095.3, 2073.8 [$Rh_6(CO)_{16}$], 2067.0, 2050.4, 2039.0, 2022.9, 1990.5 and 1966.5 cm^{-1}. A typical spectrum in

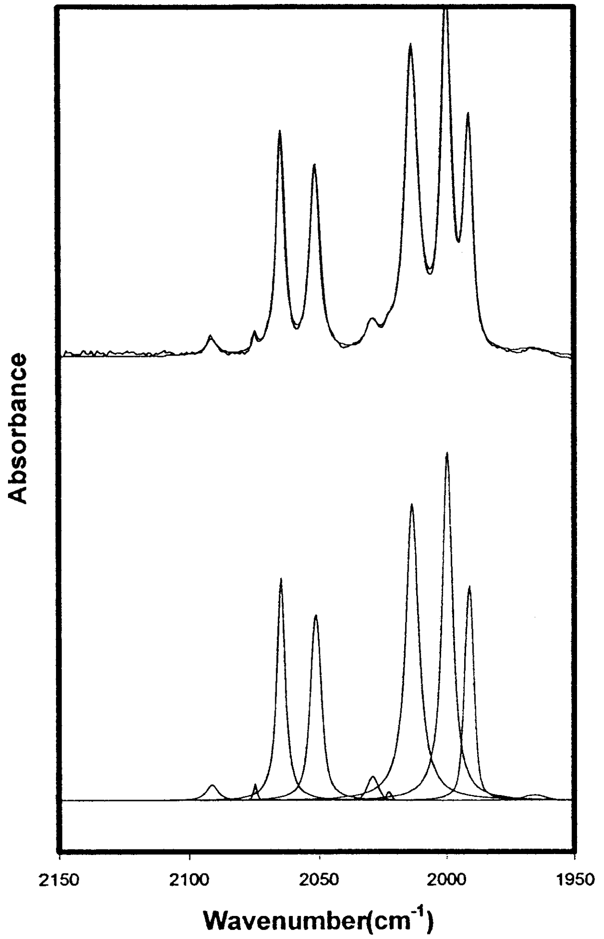


Fig. 4. Deconvolution of 2-methyl-1,3-butadiene product in the metal–carbonyl interval. Top curves represent original spectrum and best fit. Bottom curve represents the deconvolution.

the high wavenumber region is shown in Fig. 5. It can be noted that a spectroscopically asymmetric aldehyde product appeared in the low wavenumber region at 1733.6 cm^{-1}. This is indicative of more than one aldehyde product. The hydroformylation of very pure oct-4-ene at these conditions leads to only one aldehyde [5h].

Since the presence of diene impurity was assumed, the *cis* oct-4-ene was analysed over a 10 m capillary column containing HP series 5, 30μ fused silica. In addition to the *cis* oct-4-ene elution band, a few small long retention time bands were also seen. As a similar problem was previously encountered in the case of cyclohexene hydroformylations [5d], the *cis* oct-4-ene was treated with maleic anhydride under reflux conditions. Periodic GC analysis confirmed that one of the long retention time elution bands could be eliminated. The 'cleaned' *cis* oct-4-ene was then used in hydroformylation experiments. Although the initial reaction period proceeded in a normal manner, new bands again appeared in the spectra at longer reaction times. This indicated that there were probably trace quantities of unconjugated dienes in the 'cleaned' *cis* oct-4-ene which could not be removed by maleic anhydride treatment, and which then underwent double-bond migrations under hydroformylation conditions, ultimately to give conjugated dienes and the characteristic 'rhodium carbonyl/diene' IR spectra.

4. Discussion and conclusions

4.1. Cluster fragmentation: presence of mononuclear complexes

The instability of rhodium carbonyl clusters cannot be overemphasized. Indeed, under CO or syngas, $Rh_4(CO)_{12}$ readily fragements to observable quantities of $Rh_2(CO)_8$ and $Rh_6(CO)_{16}$ [4]. Furthermore, in the presence of both syngas and alkenes, mononuclear acyl rhodium tetracarbonyls are readily formed [5]. These observations are entirely consistent with the known

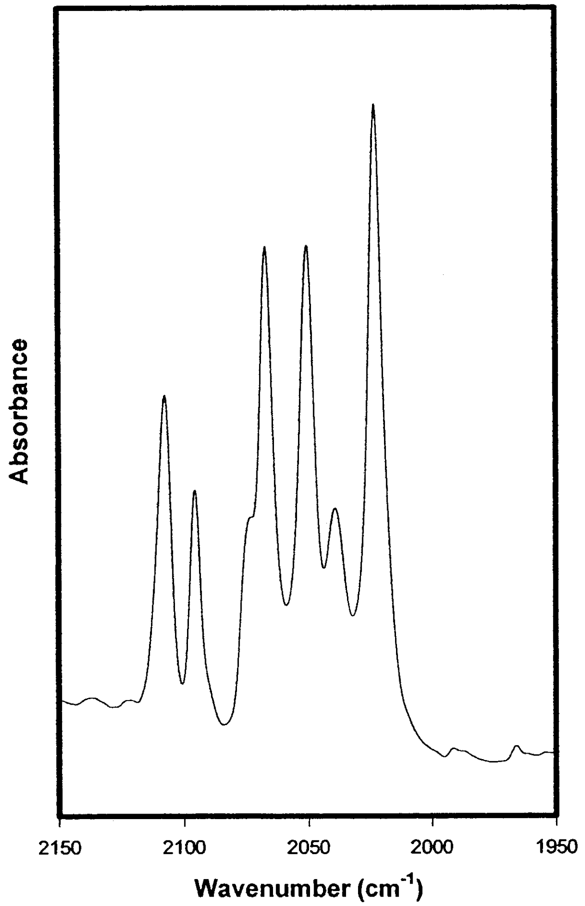


Fig. 5. In-situ high-pressure high-wavenumber IR spectra of the reaction of $Rh_4(CO)_{12}$ under syngas at 298 K with *cis* oct-4-ene poisoned by trace conjugated diene. Typical band positions: 2107.3, 2095.3, 2073.8 [$Rh_6(CO)_{16}$], 2067.0, 2050.4, 2039.0, 2022.9, 1990.5 and 1966.5 cm^{-1}.

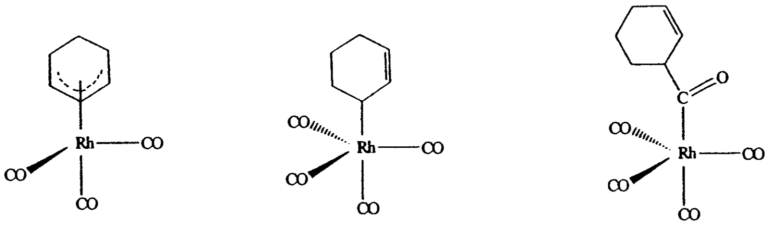


Fig. 6. Probable new observable mononuclear rhodium complexes in the hydroformylation of conjugated dienes.

thermochemistry of rhodium. Indeed, the enthalpy of formation of a rhodium–rhodium bond is only 93 kJ mol^{-1} whereas, the enthalpies of rhodium–carbon or rhodium–carbonyl bonds are in excess of 155 kJ mol^{-1} [32]. Consequently, cluster fragmentation of $Rh_4(CO)_{12}$ to mononuclear species in the presence of appropriate organic ligands under catalytic conditions is expected under a wide range of reaction conditions.

In the present case of the hydroformylation of conjugated dienes, cluster fragmentation of $Rh_4(CO)_{12}$ to lower nuclearity complexes, and specifically new mononuclear complexes, can be expected. Under syngas, $Rh_4(CO)_{12}$ will undergo cluster opening and/or fragmentation, and hydrogen activation will occur. The subsequent reaction of rhodium carbonyl hydrides, most likely hydrido rhodium tricarbonyl and/or hydrido rhodium tetracarbonyl, with conjugated dienes can be readily assumed.

4.2. The non-competitive situation

The in-situ IR spectra taken during the hydroformylations of the conjugated dienes indicated the presence of at least three new rhodium complexes. A preliminary analysis indicates that the following three sets of vibrations belong together: (A) 2051, 2029 and 1991 cm^{-1}; (B) 2000, 2013 and 2065 cm^{-1}; (C) 2108, 2061, 2037 and 2019 cm^{-1}. The latter set clearly indicates the presence of a mononuclear acyl rhodium tetracarbonyl species, although it remains unclear whether this observable acyl complex $RCORh(CO)_4$ is derived from a R = alkenyl moiety or a R = formylalkyl moiety (or is a mixture of both). The initial assumption would be that the complex is an (R = alkenyl) acyl rhodium tetracarbonyl, however, the possibility of an (R = formylalkyl) acyl rhodium tetracarbonyl cannot be ruled out.

Considering the related cobalt carbonyl chemistry as outlined in Section 1, it is very likely that η^3 allyl rhodium tricarbonyl species, σ allyl rhodium tetracarbonyl species and (R = alkenyl and/or formylalkyl) acyl rhodium tetracarbonyl are formed in the present rhodium carbonyl/diene system in observable quantities. Fig. 6 illustrates the probable three types of new observable complexes present in this study.

If CO insertion occurs in the σ allyl rhodium tetracarbonyl, and an unsaturated aldehyde is the final product of the catalysis, the catalytic cycle can be illustrated as shown in Fig. 7. It should be noted that the stereochemistry, particularly of the hydride species, may be different from than that shown.

4.3. Comparison to methylene cyclopropane hydroformylation

Recently, we reported the hydroformylations of a homologous series of methylene cycloalkanes [5h]. Although the high molecular weight members of the series underwent straightforward hydroformylation, unusual chemistry occurred when using methylene cyclopropane. Instead of obtaining just the corresponding acyl rhodium tetracarbonyl (R = alkyl) at 2110, 2064, 2038 and 2020 cm^{-1} [5h], many new bands arose. The final spectrum after deconvolution gave absorbance

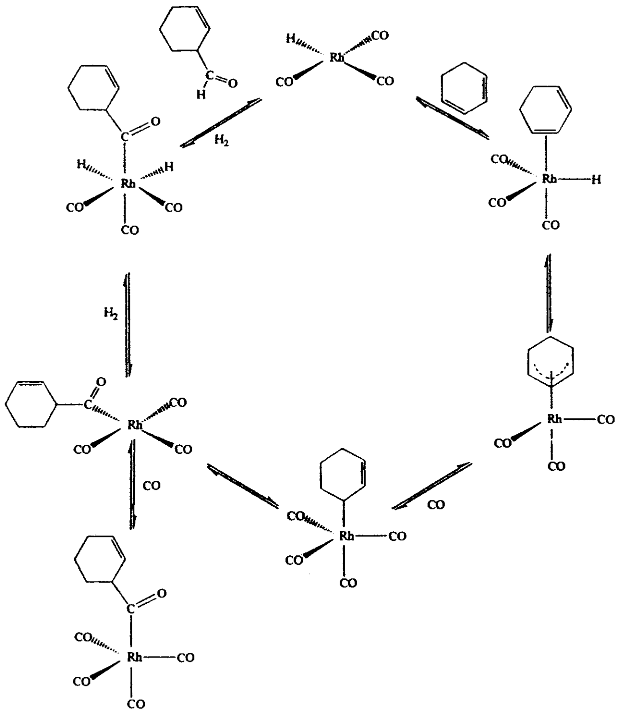


Fig. 7. Proposed unicyclic homogeneous rhodium catalytic cycle for the hydroformylation of conjugated dienes under low conversion, with presence of η^3 allyl rhodium tricarbonyl species, σ allyl rhodium tetracarbonyl species and acyl rhodium tetracarbonyl species (R = alkenyl).

maxima at 2111.9, 2104.1, 2094.2, 2073.8 [$Rh_6(CO)_{16}$)], 2066.9, 2053.6, 2046.6, 2040.9, 2034.0, 2019.7, 2016.0, 2003.9 and 1994.5 cm^{-1}.

The bands at 2094.2, 2066.9, 2053.6, 2034.0, 2019.7, 2016.0, 2003.9, and 1994.5 cm^{-1} are very similar to the spectral characteristics seen in the present study using conjugated dienes. As we suggested elsewhere [5h], we believe that attack at the α carbon atom leads to the formation of a classic acyl rhodium tetracarbonyl under hydroformylation conditions, but attack at the β carbon atom leads to ring cleavage. Ring cleavage, plus a hydrogen migration would lead to the conversion of methylene cyclopropane to 1,3-butadiene. Therefore, the formation of a conjugated diene/rhodium complex is certainly reasonable in the case of the hydroformylation of methylene cyclopropane.

4.4. The competitive situation

It was shown in the alkene hydroformylation experiments, that the presence of trace quantities of conjugated dienes drastically altered the expected chemistry and kinetics of the catalytic system. In the case of *cis* oct-4-ene tainted by conjugated dienes, in-situ IR spectra clearly showed that the expected acyl rhodium tetracarbonyl (R = alkyl) vibrations were strongly suppressed and the presence of numerous new vibrations occurred. Thus trace quantities of conjugated dienes successfully compete against an excess of alkenes for the rhodium in the system and consequently altered the hydroformylations. The affinity of conjugated dienes for rhodium is dramatically higher than the affinity exhibited by alkenes.

4.5. Additional remark concerning competitive cyclohexene hydroformylation

As mentioned, the hydroformylation of cyclohexene has been studied by this group on multiple occasions [5d,5g]. The resulting acyl rhodium tetracarbonyl (R = alkyl) has absorbance maxima at 2109, 2063, 2037 and 2019 cm^{-1}. The presence of conjugated dienes was also a problem in these experiments. However, under extensive reflux with maleic anhydride, the cyclohexene could be obtained in a very pure form. The experiments conducted with trace quantities of 1,3-cyclohexadiene gave a distinct pattern with new absorbance maxima 2086, 2062, 2046, 2024, 2006, and 1986 cm^{-1}. It appears that *cis* oct-4-ene is considerably more difficult to purify than cyclohexene.

4.6. Chemometric analysis and advanced deconvolution

The set of 2-methyl-1,3-butadiene reaction spectra (Fig. 3), obtained under different reaction conditions, suggests an unusual opportunity for further analysis. Indeed, since these spectra consist of three or more new species, the determination of the number of observable species, the number of observable reactions, and the reconstruction of each of the pure component spectra would afford considerably more insight into the homogeneous catalysis of conjugated dienes. However, as the spectra indicate, there are subtle changes in the band positions and subtle changes in the band shapes induced by the pressure and composition differences, and these problems introduce considerable mathematical complications.

Recently, we introduced an extensive theory for obtaining the number of observable species and the number of observable reactions in an arbitrary homogeneous reaction system, from the set of in-situ IR spectra alone, even in situations where the decadic absorptivities of the solutes are not constant [33]. This theory is imbedded in a statistical setting, and permits the analysis of IR spectroscopic data where band positions and band shapes change. Once the number of statistically significant species is known (goal I), reconstruction of all the individual solute spectra can be initiated (goal II). In fact, it is possible to reconstruct highly overlapping solute spectra in situations where the experimentalist has no a priori information on the individual components [34,35]. In addition, an efficient algorithm has been developed to search for all the pure component spectra in systems involving a large number of species (with no a priori pure component information) [36], and to deal with various related issues. Finally, given the results of goals I and II, and data on the initial moles of reactants in the system, it is possible to reconstruct the reaction stoichiometry of the entire reaction network (goal III).

Presently, we are in the final stages of completing the development of the set of algorithms I–III. Once a sufficient number of tests have been successfully performed on synthetic spectroscopic data, it is our intention to re-investigate the hydroformylation of 2-methyl-1,3-butadiene. Such results can be expected in a year or two.

4.7. Chemoselectivity and possible caging effects in dual-cycle systems

In the simplest case, solvent caging is exemplified by the photodissociation of I_2 in solution [37]. Upon UV irradiation, I_2 dissociates to create a caged pair. The iodine atoms will repeatedly collide, perhaps as many as 1000 times, before they undergo recombination to molecular iodine or successfully escape from their solvent cavity. In fact, the quantum efficiency for generating a separated iodine atom pair is very low, due to the large probability of recombination compared to solvent cage escape. Recently, we have been concerned with a more complicated scenario, namely the possible effect of solvent caging on selectivity [38], particularly chemoselectivity in coupled dual-cycle homogeneous catalytic systems [34b].

Coupled dual-cycle chemoselective systems are quite common in homogeneous catalysis. These include most, but not all, catalytic systems capable of performing both the hydrogenation and hydroformylation of dienes. In the present case of diene hydrogenation/hydroformylation, two distinct dual-cycle systems A and B may be involved. It is important to recognize that in both systems, the products of the first cycle are the also the initial reactants for the second cycle. Thus, the cycles are coupled by a material constraint.

Case A. The first cycle involves the reaction of a rhodium carbonyl hydride with diene to give a rhodium carbonyl hydride and an alkene as products. The second cycle involves the reaction of a rhodium carbonyl hydride with an alkene to give a rhodium carbonyl hydride and a saturated aldehyde as products. In other words, the first cycle involves hydrogenation and the second involves hydroformylation.

Case B. The first cycle involves the reaction of a rhodium carbonyl hydride with diene to give a rhodium carbonyl hydride and an unsaturated aldehyde as products. The second cycle involves the reaction of a rhodium carbonyl hydride with an unsaturated aldehyde to give a rhodium carbonyl hydride and a saturated aldehyde as products. In other words, the first cycle involves hydroformylation and the second involves hydrogenation.

Since the products for the first cycle are the initial reactants for the second cycle, for both scenarios A and B, a solvent cage effect could influence the time-dependent distribution of the organic products. Indeed, if a strong solvent cage effect exists for scenario A, little free alkene would be observed. Similarly, if a strong solvent cage effect exists for scenario B, little free unsaturated aldehyde would be observed. In fact, there is rather strong spectroscopic evidence that a solvent cage effect on chemoselectivity is occurring in the present experiments. The spectra indicate that there is little if any free alkene and/or unsaturated aldehyde in the reaction mixture during the catalysis. It should be noted that free alkene and/or unsaturated aldehyde should accumulate if there isn't as cage effect, since they are relatively unreactive compared to the conjugated dienes.

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