Note

The homogeneous rhodium catalyzed hydroformylation of ethylene starting with tetrarhodium dodecacarbonyl — the observation of a new type of rhodium carbonyl spectrum [1]

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Abstract

The homogeneous rhodium catalyzed hydroformylation of ethylene was studied, starting with $Rh_4(CO)_{12}$ in n-hexane solvent, at 293 K under 1.0–4.0 MPa CO, 0.5–2.0 MPa H_2 and 0.5–5.0 MPa C_2H_4. The analytic method was in situ high-pressure infrared spectroscopy. Two different metal carbonyl spectra were observed during the course of the active hydroformylations. One spectrum, observed primarily at high CO partial pressures, corresponds exactly to the well-documented mononuclear acyl rhodium tetracarbonyl (2112, 2068, 2038, 2020 cm^{-1}). The other spectrum, observed primarily at low CO partial pressures, has absorbance maxima at 2089, 2038 and 2017 cm^{-1}. It is tentatively suggested that the latter spectrum may belong to the elusive ethyl rhodium tetracarbonyl. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous, in situ spectroscopic studies related to the unmodified rhodium carbonyl catalyzed hydroformylation of alkenes have been reported. These include studies of $Rh_4(CO)_{12}$ under syngas and the observations of $HRh(CO)_4$ and $Rh_2(CO)_8$ [1], hydroformylation with ethylene [2], hydroformylations and associated kinetic studies with 3,3-dimethylbut-1-ene, cyclohexene and styrene [3], as well the characterization of over 20 mononuclear acyl rhodium tetracarbonyls [4]. Mononuclear acyl rhodium tetracarbonyls $RCORh(CO)_4$ have characteristic infrared absorbance maxima at ca. 2110, 2063, 2037, 2020 and 1700 cm^{-1}, whether derived from terminal or internal alkenes, cycloalkenes or methylene cycloalkanes.

In all of our previous studies of the unmodified rhodium carbonyl catalyzed hydroformylation of alkenes, high quality in situ spectra could be obtained, with high signal-to-noise ratios. Furthermore, in almost all of our previous studies, observable quantities of acyl rhodium tetracarbonyls were readily formed under hydroformylation conditions, to the exclusion of other observable rhodium carbonyl intermediates. The two notable exceptions were experiments performed with methylene cyclopropane and ethylene. With methylene cyclopropane, cleavage of the cyclopropyl ring occurred and an exceedingly complex spectra resulted [4].

King et al. [2] observed infrared absorbance maxima at 2115, 2037 and 2019 cm^{-1} during the hydroformylation of ethylene under considerable CO partial pressure. Our studies with ethylene have shown that this system is extremely difficult to study spectroscopically, and produce considerably more complex spectra then anticipated. Given the considerable importance of ethylene in hydroformylations, it is the purpose of the present contribution to document our preliminary efforts with ethylene as substrate.

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[1] Primary experimental research performed at ETH-Zurich 1992–1995. Analysis performed at NUS 1999.

2. Experimental

2.1. General information

All solution preparations were carried out under argon (99.999% Pan Gas AG, Luzern, Switzerland) using standard Schlenk techniques [5]. 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-Angstrom 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) 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) and was used without further purification-although trace quantities of the high nuclearity cluster $Rh_6(CO)_{16}$ is virtually always present. The complex $Rh_4(CO)_{12}$ is known to be oxygen, water and light sensitive [6]. The *n*-hexane solvent (stated purity 99.6%, Fluka AG) was refluxed over sodium potassium alloy under argon. Ethylene with purity of 99.9% min (Pan Gas) was used as delivered.

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 infrared cell. The autoclave ($P_{max} = 22.5$ MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model 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 in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, consisting of autoclave, pump, transfer lines and infrared cell, was cooled using a Lauda RX20 cryostat 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 in. (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 infrared cell was constructed at the ETH-Zürich of SS316 steel and could be heated and cooled. The CaF_2 single crystal windows (Korth Monokristalle, Kiel Germany) had dimensions of 40 mm diameter by 15 mm thickness. Two sets of Viton and silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow through cell [7], is a variation on a design due to Noack [8], and differs in some respects from other high-pressure infrared cells described in the literature (for a review, see Whyman [9]). The high-pressure cell was situated in a Perkin–Elmer 983 infrared spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A schematic diagram of the experimental setup can be found in reference [3d].

2.3. In situ spectroscopic studies

All experiments were performed in a similar manner. First, ca. 150 ml hexane was transferred to the autoclave and single beam spectra were recorded. Ethylene was added and spectra were taken, then CO was added and more spectra were taken. Then a solution of ca. 100 mg $Rh_4(CO)_{12}$ dissolved in 50 ml *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO and then add to the autoclave. Again spectra were taken. Hydrogen was added to start reaction and periodic spectra taken in the range 1600–2200 cm^{-1}.

3. Results and discussion

As already mentioned in the experimental section, a wide range of reaction conditions were employed, in order to find conditions under which observable quantities of new rhodium complexes/intermediates could be observed. To summarize, high partial pressures of CO gave rise to faster conversion of the precursor $Rh_4(CO)_{12}$, and produced spectra with predominantly the acyl rhodium carbonyl complex $RCORh(CO)_4$ (R = $-CH_2CH_3$). At low CO partial pressures, a distinct and previously unobserved three terminal CO IR pattern emerged. Also, higher ethylene concentrations assisted the rapid transformation of $Rh_4(CO)_{12}$. Increased hydrogen partial pressures increased the rate of conversion of ethylene.

The most serious spectroscopic problem arose from the simultaneous use of three gases in this reaction system. In particular, the addition of CO or H_2 gave rise to changes in the solubility of ethylene and more importantly, gave rise to changes in the band center positions and band shapes of ethylene. Therefore, it proved very difficult to produce good reference spectra for spectral subtraction purposes. Moreover, the solubility of ethylene in hexane is very high, thus increasing

the liquid-phase reaction volume significantly, and reducing the nominal rhodium concentrations accordingly (leading to weak carbonyl absorbance bands). Taken together, all of these complications make a detailed kinetic analysis extremely difficult.

Our results concentrate primarily on the high versus low CO partial pressure reaction conditions. Fig. 1 presents a reference spectrum of ethylene, a spectrum of the reaction solution when gases are released (to show the instability of the rhodium carbonyls present), a spectrum at low CO partial pressure and a spectrum at high CO partial pressure. The high CO partial pressure spectrum (D) clearly shows the presence of the acyl rhodium tetracarbonyl $RCORh(CO)_4$ (R = $-CH_2CH_3$) as well as additional vibrations. At low CO partial pressures, a distinct three band absorbance pattern emerges (C). It appears, upon raising or lowering the CO partial pressure, that the acyl rhodium tetracarbonyl $RCORh(CO)_4$ (R = $-CH_2CH_3$) and the new species readily interconvert.

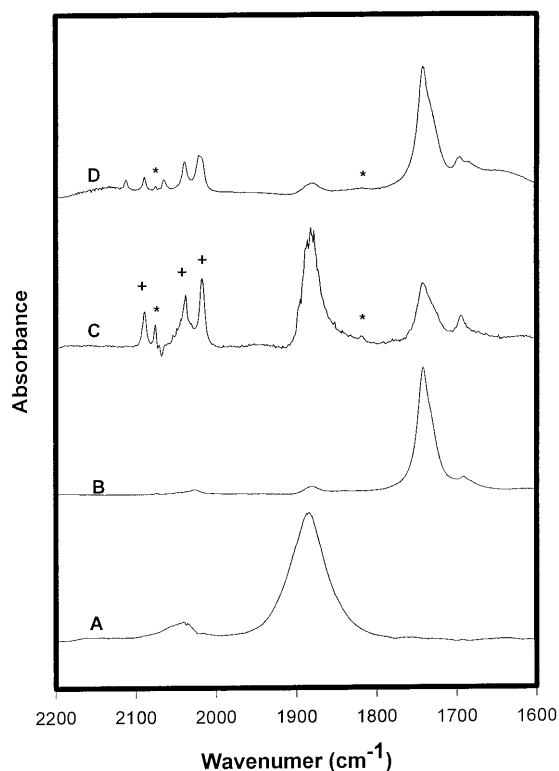Spectrum C appears to have little or no $Rh_4(CO)_{12}$ present, but it does have absorbance due to $Rh_6(CO)_{16}$

Fig. 1. In situ high-pressure infrared spectra of the reaction of $Rh_4(CO)_{12}$ under syngas at 293 K and in the presence of ethylene. (a) Reference of dissolved ethylene (hexane subtraction); (b) reaction solution after most gaseous components are released (hexane subtraction); (c) reaction solution at ca. 3 bar CO, 3 bar H_2 and 40 bar ethylene after 24 h (hexane subtraction and best ethylene subtraction, * is $Rh_6(CO)_{16}$, + is new species); (d) reaction solution at ca. 40 bar CO, 5 bar H_2 and 10 bar ethylene after 24 h (hexane subtraction and best ethylene subtraction, * is $Rh_6(CO)_{16}$).

as seen by the bands at 2073 and 1818 cm^{-1}. Also, given the high partial pressure of ethylene used, there are broad absorbance at ca. 2035 and 1885 cm^{-1}. If further subtraction of ethylene had been performed, a classic sigmoid curve would have resulted due to the differences between the reference ethylene spectrum and ethylene under reaction conditions. The propanal has absorbance at ca. 1730 and 1700 cm^{-1}, respectively. This leaves three primary absorbance bands in the terminal CO region at 2089, 2038 and 2017 cm^{-1}. We have never before seen such an infrared absorbance pattern when using $Rh_4(CO)_{12}$ under hydroformylation conditions. It is the absorbance at 2089 cm^{-1}, which is particularly unusual.

As we have shown on so many occasions, $Rh_4(CO)_{12}$ reacts under hydroformylation conditions to readily yield mononuclear intermediates. Given the complete transformation of $Rh_4(CO)_{12}$ in the presence of ethylene to give primarily $RCORh(CO)_4$ (R = $-CH_2CH_3$), along with the rapid interconversion of $RCORh(CO)_4$ with the new species, it stands to reason that the unknown species is almost certainly mononuclear. Indeed, no bridging carbonyls are apparent, and the terminal CO region is very simple. Assuming a mononuclear and coordinatively saturated nature for the unknown species, the three band structure at 2089, 2038 and 2017 cm^{-1} strongly suggests a C_{3v} symmetry like that existing in the trigonal bipyramid structures $HCo(CO)_4$ and $CH_3Co(CO)_4$ [10], $ClHgCo(CO)_4$, $BrHgCo(CO)_4$ and $IHgCo(CO)_4$ [11], as well as many other monosubstituted pentacoordinated carbonyl complexes [12]. In this regard it can be noted that the carbonyl bands for $CH_3Co(CO)_4$ are at 2105, 2036 and 2019 cm^{-1}. $HRh(CO)_4$ has carbonyl absorbance at 2070, 2039 and 2008 cm^{-1}.

Although there is some absorbance in the reaction spectra at ca. 1700 cm^{-1}, this is apparently not associated at all with the species giving rise to the pattern a 2089, 2038 and 2017 cm^{-1} [13]. Indeed, if the new species were an acyl rhodium tetracarbonyl with the acyl group in a radial position rather than an axial position, the planar –COR group would cause a breakdown in overall symmetry. C_s symmetry would result accompanied by four terminal CO vibrations. (The axially substituted acyl rhodium tetracarbonyl also has C_s symmetry and four terminal CO vibrations). In light of the above discussion, we tentatively assign the new species with absorbance at 2089, 2038 and 2017 cm^{-1} as an ethyl rhodium tetracarbonyl $RRh(CO)_4$ (R = $-CH_2CH_3$). Given the infrared spectroscopic diffculties associated with these ethylene hydroformylations, high-pressure NMR measurements would appear to be the most reliable method of confirming the identity of this new species.

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[13] One reviewer suggested the possible existence of a species $EtC(O)Rh(CH=CH_2)(CO)_3$. Such a species could be anticipated to have three terminal CO vibrations, a vibration in the acyl region and an alkene vibration. As already mentioned, the vibration at 1700 cm^{-1} does not seem to be related to the new complex.