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Isotope Effects in the Hydroformylation of Olefins with Cobalt Carbonyls as Catalysts

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The stoichiometric hydroformylation reaction has been shown to consist of two variations: conducted in the presence of stoichiometric amounts of $HCo(CO)_4$ and CO (Type I) or in the presence of $Co_2(CO)_8$ and H_2 (Type II). The main difference between these two types of stoichiometric hydroformylation reactions was believed to be the nature of the cobalt carbonyl precursor and the number of steps necessary to the onset of reaction. In both types of reactions, however, the source of the hydrogen in the hydrogenolysis step was considered to be $HCo(CO)_4$ and not H_2. In this article, we examine the conventional assumptions regarding the nature and mechanism of the hydrogenolysis step for both types of stoichiometric hydroformylation reactions. This examination stems from inconsistencies observed during the study of the mechanism of the second type of the stoichiometric hydroformylation reaction, which cast some doubt on the identification of $HCo(CO)_4$ as the hydrogen-donor species, under conditions in which molecular hydrogen is present. The presence of isotope mixtures of H_2/D_2 in the gas phase during the various steps of the reaction showed that the ratio of H/D isotopes in the hydrocarbon portion of the aldehydic product correlates with the $HCo(CO)_4/DCo(CO)_4$ ratio in solution, while the R(CO)H/R(CO)D product ratio correlates with the H_2/D_2 in the gas phase. Hence, the dominant reaction pathway for the hydrogenolysis step in this type of stoichiometric hydroformylation reaction is the direct reaction of hydrogen or deuterium with the acyl complex intermediate.

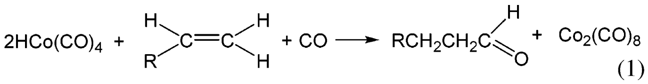
1. Introduction

The hydroformylation reaction, first discovered by Roelen in 1938,[1] was the first important homogeneous transition-metal catalyzed reaction. The basic reaction involves the conversion of olefins to aldehydes in the presence of a mixture of carbon monoxide and hydrogen (synthesis gas) using cobalt catalysts. When the hydroformylation reaction is carried out at 150−200 °C and 100−150 atm of synthesis gas, almost any form of cobalt acts as a catalyst precursor for the reaction, such as cobalt carbonate, cobalt acetate, etc. Under the conditions of the reaction, the Co^{II} salt is reduced by hydrogen to Co^0, followed by a reaction with CO, which leads to the formation of $Co_2(CO)_8$. Subsequently, in the presence of molecular hydrogen under the conditions of the high temperatures and pressures, the $Co_2(CO)_8$ is converted to $HCo(CO)_4$, which is believed to be the pivotal active catalyst in the reaction.[2−4]

When the aldehyde synthesis is carried out at high temperature and high pressure of synthesis gas with a small quantity of cobalt responsible for converting considerable large amounts of olefin to produce aldehyde, the reaction is purely catalytic. On the other hand, when the aldehyde synthesis is carried out at room conditions using $Co_2(CO)_8$ or $HCo(CO)_4$ in stoichiometric concentrations, the reaction is considered stoichiometric. Despite these differences, it became clear relatively early that the stoichiometric reaction and the catalytic reaction were very closely related. Some studies report, for example, that under catalytic conditions more than 50% of the cobalt is converted to $HCo(CO)_4$ during the course of the reaction.[2] It was further shown that, in the stoichiometric reaction, the relative rates of disappearance of $HCo(CO)_4$, using the olefins 1-hexene, 2-hexene, and cyclohexene,[3] were 13:6:1, in reasonably good agreement with the relative rates of reaction of these same olefins in the catalytic hydroformylation.[5] It seemed clear, therefore, that mechanistic information obtained from the stoichiometric reaction conveniently conducted at room conditions was applicable to the catalytic reaction.

The different types of stoichiometric hydroformylation reactions that were investigated have been reviewed by Pino, Piacenti, and Bianchi.[6] We shall mainly concern ourselves with the two main types of stoichiometric reactions, which were carried out either in the presence of stoichiometric amounts of preformed $HCo(CO)_4$ and CO (Type I)[7] or in the presence of stoichiometric amounts of $Co_2(CO)_8$ precursor and hydrogen (Type II).[8]

The overall reaction with preformed $HCo(CO)_4$ is shown in eq 1:



(1)

In one of the early studies of the stoichiometric reaction in which the absorption of CO was monitored,[7] it was shown that

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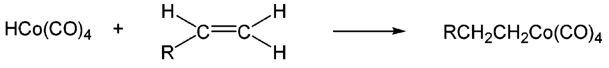
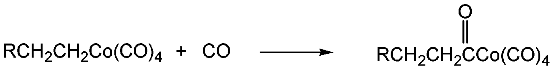
the stoichiometry of the reaction could be explained by the following reaction sequence:[7−9]

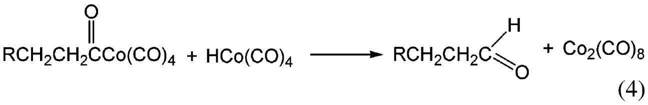


(2)



$$RCH_2CH_2Co(CO)_4 + CO \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_4$$

(3)

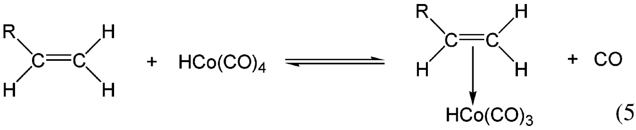


(4)

Under certain conditions, there was a reasonable correspondence between the rates of $HCo(CO)_4$ disappearance and the absorption of carbon monoxide.

The first step in the reaction is suggested to be the first-order dissociation of the $HCo(CO)_4$ to the coordinatively unsaturated $HCo(CO)_3$, possessing a ligand vacancy. This hypothesis of dissociation prior to olefin complexation[10] has received support from the kinetic work of Ungváry[11] on the decomposition of $HCo(CO)_4$ and the matrix isolation work of Orchin et al.,[12] where infrared evidence is presented in support of the existence of $HCo(CO)_3$.

It is, of course, well-known that CO has an inhibiting effect on the rate of hydroformylation.[13,14] Thus, under identical conditions at 0 °C, except for the presence of 1 atm of CO as compared to 1 atm of N_2, the reaction performed under N_2 is complete in a few minutes, while that under CO takes several hours.[15] However, other steps in the mechanism involve a CO-deficient species and hence may be inhibited by the presence of this gas. The S_N2 type of reaction in which the olefin displaces a CO ligand, shown in eq 5, cannot be ruled out, even though the transition state for such a process involves six-coordinated cobalt with oxidation number one. Possibly, the availability of many low-lying antibonding orbitals furnished by the highly unsaturated ligands would make such a transition state energetically accessible.[9,16]



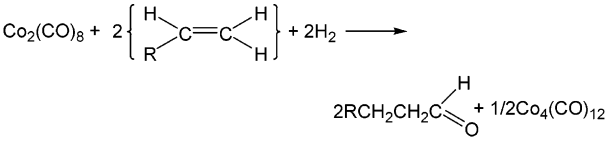
(5)

Equation 2 is an example of olefin insertion into a M−H bond, and its reverse reaction is an example of β-hydrogen elimination. In this context, we should mention that the first alkyl cobalt complex that has been characterized was $CH_3Co(CO)_4$,[17] but it decomposed even at −35 °C and of course could not be formed from an olefin precursor. Other alkyl cobalt carbonyls, such as ethyl or benzyl cobalt carbonyls[18] have also been identified.[19,20] The conversion of an alkyl cobalt carbonyl to an acylcobalt carbonyl[21] has substantial precedent. Work with $CH_3Mn(CO)_5$ and labeled CO[16,22,23] has shown that the acyl carbon atom is generated from one of the carbonyl groups already coordinated to the metal and is definitely not the entering CO molecule. In the reverse reaction, labeling of the acyl carbon has shown that the label remains in the alkyl metal carbonyl and the ejected CO is one of the CO ligands on the metal. The same type of mechanistic study was done indirectly with cobalt,[16,18,24] and the results suggest that the acyl formation proceeds via the same mechanism as for the manganese. Other ligands with nucleophilic character such as phosphates,[20,25,26] triphenylphosphines,[25,27] primary amines,[25] and iodide ions[28−30] can promote this alkyl-acyl conversion and may be regarded as either a CO insertion into the R−M bond or a rearrangement of the alkyl group to one of the coordinated CO ligands. The existing evidence is interpreted by Noack and Calderazzo as indication for an alkyl migration rather than a CO insertion,[22] but the problem has not yet been definitively settled.

The hydrogenolysis of acylcobalt carbonyls, eq 4, is strongly inhibited by CO.[31] A first-order dissociation of the acylcobalt tetracarbonyl to CO and tricarbonyl has been proposed as the rate-determining step. Presumably in the presence of CO, the predominant species is a pentacoordinated cobalt with no readily accessible sites on the Co atom for hydrogen-donor molecules. However, at low CO pressure, the complex may lose one CO group, leading to an appreciable concentration of coordinatively unsaturated complex and thus permitting interaction between the metal and the hydrogen donor. In the stoichiometric reaction with preformed $HCo(CO)_4$, the hydrogenation step must be achieved by $HCo(CO)_4$ or $HCo(CO)_3$. If both the acyl and the hydrocarbonyl are in the five-coordinated state, the reaction will be slow. The hydrogenolysis of the acylcobalt carbonyl by $HCo(CO)_4$ or $HCo(CO)_3$ can be written at least in a formal way, analogously to the decomposition of $HCo(CO)_4$ to $Co_2(CO)_8$.[32,33]

The aldehyde formation step has been subject to different opinions concerning the actual hydrogenating agent. Kirch and Orchin[7] have found that 1 mol of CO was consumed for 2 mol of $HCo(CO)_4$. This result was interpreted as confirming the mechanism in which $HCo(CO)_4$ reacts with the acylcobalt complex to give aldehyde and $Co_2(CO)_8$. However, this mechanism is correct only for a pure stoichiometric hydroformylation where the only source of hydrogen is $HCo(CO)_4$.

The second type of stoichiometric hydroformylation at room temperature was performed using $Co_2(CO)_8$ in stoichiometric amounts as the starting cobalt complex instead of $HCo(CO)_4$. The reaction was performed in hydrocarbon solvents at elevated hydrogen pressure[8] and corresponded to the following stoichiometry:



(6)

The $Co_2(CO)_8$ complex is the only source of carbon monoxide, which is liberated during the $Co(CO)_4 \rightarrow Co(CO)_3$ transformation. Therefore, two molecules of $Co_2(CO)_8$ are involved in the reaction, and $Co_4(CO)_{12}$ is quantitatively recovered upon completion.

In the absence of CO, the reaction proceeds immediately at room temperature, after the H_2 has been added. However, in the presence of CO, a long induction period was noticed even at low CO partial pressures.[8] Since a retarding effect of CO under the same conditions was also found in the synthesis of $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2 in the absence of olefins,[34−36] it was assumed that as a first step in the stoichiometric hydroformylation reaction, $Co_2(CO)_8$ reacts with H_2 via the $Co_2(CO)_7$ coordinatively unsaturated intermediate to form $HCo(CO)_4$. This latter compound, as already described, would then hydroformylate the olefin by a mechanism that is similar to the one described for the reaction with preformed $HCo(CO)_4$.

Hence, the main difference between these two types of stoichiometric hydroformylation reactions was believed to be the nature of the cobalt carbonyl precursor and the number of steps necessary to the onset of reaction. In both types of reactions, however, the source of the hydrogen in the hydrogenolysis step was believed to be achieved via the interaction of the acylcobalt complex and $HCo(CO)_4$.

In this article, we examine the conventional assumptions regarding the nature and mechanism of the hydrogenolysis step for both types of stoichiometric hydroformylation reactions. This examination stems from inconsistencies observed during the study of the mechanism of the second type of the stoichiometric hydroformylation reaction, which cast some doubt on the identification of $HCo(CO)_4$ as the hydrogen-donor species, under conditions in which molecular hydrogen is present.

2. Experimental Methods

2.1. Hydroformylation of Olefin with a Mixture of $HCo(CO)_4/DCo(CO)_4$ and H_2. $Co_2(CO)_8$ (1.9311 g) was dissolved in 650 mL of isooctane that was pretreated with $LiAlH_4$ and redistilled under N_2 atmosphere. The solution was introduced by suction into a 1-L stainless steel autoclave with exclusion of air. The reaction started when 80 atm of 1:1 gas mixture of D_2/H_2 was pressurized into the system. No initial CO was added. The reaction was carried out at 31 °C. A sampling tube reaching the bottom of the reaction autoclave was connected directly to a flow-through high-pressure/high-temperature infrared cell.[54,55] Before each spectrum was scanned, the cell was flushed with 10−15 mL of fresh solution from the autoclave by opening a discharge valve placed after the cell. After each sampling cycle, the autoclave was re-pressurized with the 1:1 D_2/H_2 gas mixture to maintain constant pressure. Before the olefin was added, the reaction solution was allowed to reach equilibrium and contained 1.976 mmol/L $DCo(CO)_4$, 4.310 mmol/L $HCo(CO)_4$, 2.874 mmol/L $Co_2(CO)_8$, and 1.385 mmol/L $Co_4(CO)_{12}$. The total volume of the equilibrated cobalt carbonyl mixture remaining in the autoclave was 500 mL.

At this point, 16 mL of 3,3-dimethylbutene (DMB) was introduced into the system, corresponding to a total amount of 125 mmol. The gas in the autoclave was flushed out and replaced by 100 atm of H_2 only. The total pressure was maintained constant in the whole system by simultaneously re-pressurizing the autoclave with H_2. The reaction was completed after 49 h. The amount of aldehyde formed corresponded to 5.9 mmol, and 116 mmol of olefin remained unreacted. At the end of the reaction all cobalt was in the form of $Co_4(CO)_{12}$, which reached a concentration of 4.289 mmol/L. Infrared spectra were recorded on a Grating Perkin-Elmer model 325 with a resolution of $\sim$0.9 cm^{-1} and on a Grating Perkin-Elmer model 983G, microprocessorized with Data Station model 3600, resolution $\sim$0.5 cm^{-1}.

All the aldehyde was of the type $(CH_3)_3C(CH_2)_2CHO$. No detectable amount of aldehyde of the type $(CH_3)_3C(CH_2)_2CDO$ was formed. At this point, the gas was released, and the autoclave was re-pressurized with 100 atm of D_2 only. The solution was kept under these conditions for 1 week. The aldehyde remained of the type $(CH_3)_3C(CH_2)_2CHO$ without any traces of its deuterated counterpart.

2.2. Hydroformylation of Olefin with a Mixture of $HCo(CO)_4/DCo(CO)_4$ and 1:1 D_2/H_2. $Co_2(CO)_8$ (1.8478 g) was dissolved in 750 mL of isooctane that was pretreated in the same way as described in section 2.1. The solution was introduced into a 1-L stainless steel autoclave by suction. The reaction started when the system was pressurized by 100 atm of 1:1 mixture of D_2/H_2 at 31 °C. After 72 h, the remaining 550 mL of solution (200 mL was used to periodically sample the progress of the reaction, as described in section 2.1.) contained 6.994 mmol/L $HCo(CO)_4$, 0.565 mmol/L $DCo(CO)_4$, 2.328 mmol/L $Co_2(CO)_8$, and 0.859 mmol/L $Co_4(CO)_{12}$. No initial CO was added.

At this point, 20 mL of DMB was introduced into the system, corresponding to a total amount of 154 mmol. The same gas was used also for hydroformylation.

The reaction was completed after 45 h. The amount of aldehyde obtained corresponded to 7.6 mmol, where 3.8 mmol were of the type $(CH_3)_3C(CH_2)_2CHO$ and 3.8 mmol were of the type $(CH_3)_3C(CH_2)_2CDO$. A quantity of 145 mol of olefin remained unreacted. At the end of the reaction, all cobalt was in the form of $Co_4(CO)_{12}$. All sampling procedure and infrared analysis were performed as described in section 2.1.

2.3. Hydroformylation of Olefin with a Mixture of $HCo(CO)_4/DCo(CO)_4$ and D_2. $Co_2(CO)_8$ (1.5764 g) was dissolved in 380 mL of isooctane pretreated in the same manner described in section 2.1. A quantity of 250 mL of this solution was transferred by suction into a 300-mL stainless steel autoclave, and reaction was started when the system was pressurized with 35 atm D_2 and 4 atm CO. The reaction was carried out at 60 °C.

Before the addition of the olefin, the remaining 200 mL of solution contained 5.21 mmol/L $HCo(CO)_4$, 3.09 mmol/L $DCo(CO)_4$, 7.79 mmol/L $Co_2(CO)_8$, and 0.336 mmol/L $Co_4(CO)_{12}$. DMB (4.6 mL) was added to the system, constituting an amount of 35.6 mmol. Since during the first period of sampling the pressure was replaced only by D_2, the partial pressure of CO in the system constantly decreased.

The reaction was completed after 28 h at 40 °C. At the end of the reaction all the cobalt was in the form of $Co_4(CO)_{12}$. The amount of aldehyde formed was 12.4 mmol, and 22.7 mmol of olefin remained unreacted. All the aldehyde was of the type $(CH_3)_3C(CH_2)_2CDO$, and no aldehyde of the type $(CH_3)_3C(CH_2)_2CHO$ was detected. All sampling procedure and infrared analysis were performed as described in section 2.1. After the completion of the reaction, the gas was released and the autoclave was re-pressurized with 100 atm of H_2 only. The solution was kept under these conditions for 1 week. The aldehyde remained as $(CH_3)_3C(CH_2)_2CDO$, without any traces of $(CH_3)_3C(CH_2)_2CHO$.

2.4. The Determination of ϵ_{max} of RC(O)D at 1714 cm^{-1}. A catalytic hydroformylation of DMB was carried out using $RhCl(CO)(PPh_3)_3$ as catalyst. A quantity of 300 mg of the catalyst was dissolved in 150 mL of pretreated hexane. DMB (5 mL) was added, and the autoclave was closed and placed in a shaking electrical oven. The reaction was carried out at 100−120 °C under a total pressure of 80 atm: 40 atm CO and 40 atm D_2. The reaction was stopped after 18 h, the autoclave was cooled to room temperature, and the excess of gas was collected into a gasometer. The liquid phase was filtered, and the product was collected by distillation under a vacuum of $\sim$100 Torr, at T = 59−60 °C. The measured density was 0.85 at room temperature. The synthesis of the nondeuterated aldehyde was carried out under identical conditions with the exception of the gas phase, which in this case was composed of 40 atm of CO and 40 atm of H_2. Mixtures of the two solutions in different ratios were used to measure and calculate the molar extinction coefficient of the deuterated aldehyde.

Infrared spectra of the aldehyde products were recorded on a Fourier transform, Nicolet model 7199, equipped with an MCT detector cooled with liquid N_2 and on a Fourier transform Nicolet Nexus 870. NMR spectra of the aldehyde products were recorded on a Bruker ARX 300 Hz, and the mass spectra were recorded on a VG Instruments 70SE mass spectrometer.

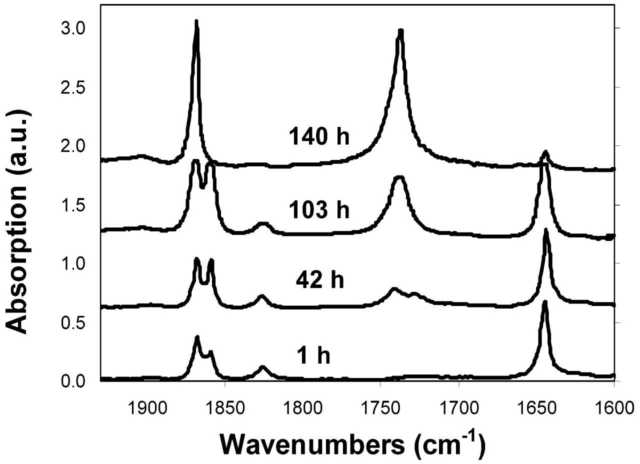


Figure 1. Time-dependent infrared spectra of the hydroformylation reaction showing the initial increase of the 1858 cm^{-1} absorption band corresponding to the increase in the concentration of $Co_2(CO)_8$ during the reaction.

3. Results and Discussion

The progression of a typical stoichiometric hydroformylation reaction with $Co_2(CO)_8$ and H_2 was monitored by infrared spectroscopy, and the sequential spectra are shown in Figure 1. The olefin DMB was introduced into a pre-equilibrated solution containing $HCo(CO)_4$, $Co_2(CO)_8$, and $Co_4(CO)_{12}$, which was achieved by the reaction of $Co_2(CO)_8$ with H_2. The considerable increase in the concentration of $Co_2(CO)_8$ upon the introduction of the olefin, as evidenced by an increase in the 1858 cm^{-1} infrared absorption band,[37,38] is inconsistent with the expected mechanistic assumptions regarding the mechanism of this reaction. The formation of $Co_2(CO)_8$ could be explained only by the long-held assumption that the hydrogenolysis of the acylcobalt carbonyls is carried out by $HCo(CO)_4$ to give aldehyde and $Co_2(CO)_7$ and finally, in the presence of CO, $Co_2(CO)_8$. However, if the reaction is carried out with $Co_2(CO)_8$ and H_2, the source of CO is the carbonyl complex, promoting the $Co(CO)_4 \rightarrow Co(CO)_3$ transformation, contrary to the observed results. Therefore, a thorough study of the hydrogenolysis step was undertaken to establish the exact nature of the hydrogen-donor molecule and the mechanism of hydrogen activation.

During some catalytic experiments carried out in our laboratory concerning the hydroformylation of ethylene with cobalt catalysts with a 1:1 gas mixture of H_2/D_2,[37] it was observed that the aldehydic hydrogen atom was 50% deuterium, in direct correlation with the composition in the gas phase. This meant that there was no detectable isotope effect concerning the aldehydic H atom, and that at least in the catalytic reaction, the hydrogenolysis step is performed directly by the H_2 molecule. This result represented the impetus to perform some stoichiometric hydroformylation reactions of Type II using gas mixtures of H_2/D_2 and, with the use of our high-pressure infrared spectroscopic equipment, to have a deeper insight on the possible isotopic effects that might occur during the course of the reaction. The various types and extents of these isotope effects can give an indication as to the species responsible for the hydrogenolysis step.

3.1. Determination of the Molar Extinction Coefficient of RC(O)D at 1714 cm^{-1}. Because of very fast H/D exchange that occurs in the formation of the hydride species of the active catalyst in the hydroformylation reaction,[39] it is not possible to obtain a purely deuterated aldehyde using this synthesis method. This is in part due to the presence of a very thin water film on the surface of the reaction vessel that cannot be removed with the conventional methods for the elimination of water traces during the reaction. Hence, the aldehyde synthesized via a catalytic hydroformylation in the presence of D_2 is a mixture of both the deuterated aldehyde group (majority product) and the regular aldehyde group (minority product). The infrared spectrum of the mixture of deuterated and regular aldehydes showed two aldehydic carbonyl bands at 1736 cm^{-1} and 1714 cm^{-1} with the ratio of 1:2, respectively, corresponding to a RC(O)H/RC(O)D ratio of 1:2. The NMR spectrum with and without internal standard (dioxan), shown in Figure 2, confirmed the above ratio. The NMR spectrum without internal standard, where the band for $(CH_3)_3{-}C$ at 0.91 ppm was used as reference, gave a ratio of 35% RC(O)H and 65% RC(O)D. The NMR spectrum with dioxan as internal standard having a band at 3.7 ppm gave the ratio of 31% RC(O)H and 69% RC(O)D.

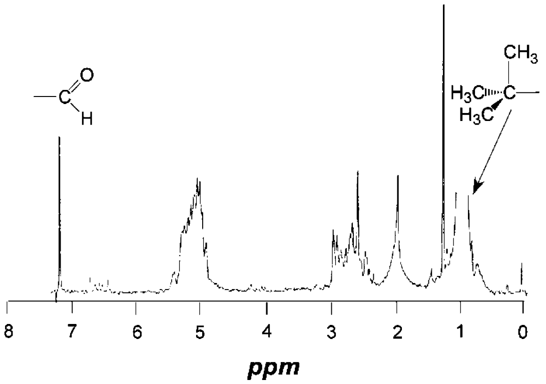


Figure 2. NMR spectrum of a mixture of $(CH_3)_3C(CH_2)_2CHO$ and $(CH_3)_3C(CH_2)_2CDO$ synthesized by the catalytic hydroformylation of 3,3-dimethylbutene in the presence of $RhCl(CO)(PPh_3)_3$ as catalyst, and 80 atm 1:1 CO/D_2 as the gas phase.

Separately, the nondeuterated aldehyde, RC(O)H, was synthesized in the same way and was obtained in pure form. This aldehyde was now used as an internal standard to prepare mixed solutions of both types of aldehydes in different ratios: 1:2, 1:1, 2:1. The infrared spectra of these solutions were measured, as shown in Figure 3, and the ratios between the 1736 cm^{-1} and 1714 cm^{-1} were calculated as the percentage of the total absorption and plotted as function of the percentage of one type of aldehyde with respect to the total aldehyde in the solution (x_D), as shown in Figure 4. The molar extinction coefficient of the deuterated aldehyde at 1714 cm^{-1}, ϵ_D, is now calculated based on the known extinction coefficient of the regular aldehyde at 1736 cm^{-1}, ϵ_H, as shown in the following relationship:

$$\epsilon_D = \epsilon_H \cdot \frac{R(1 - x_D)}{1 - R{\cdot}x_D}$$

where

$$R = \frac{(\mathrm{Abs_D}/(\mathrm{Abs_D} + \mathrm{Abs_H}))}{c_D/(c_D + c_H)};$$

$$\mathrm{Abs_D} = \epsilon_D{\cdot}c_D{\cdot}d \text{ and } \mathrm{Abs_H} = \epsilon_H{\cdot}c_H{\cdot}d$$

c_D and c_H are the concentrations of the deuterated and regular aldehyde, respectively. Finally,

$$x_D = \frac{c_D}{c_D + c_H}$$

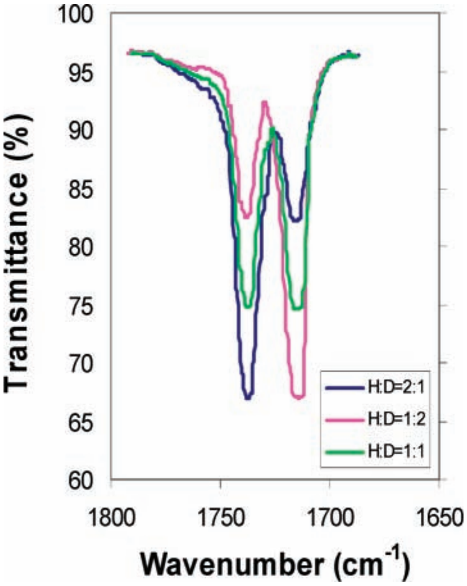


Figure 3. Infrared spectra of several mixtures of $(CH_3)_3C(CH_2)_2CHO$ and $(CH_3)_3C(CH_2)_2CDO$, corresponding to 1:2, 1:1, and 2:1 ratios, respectively.

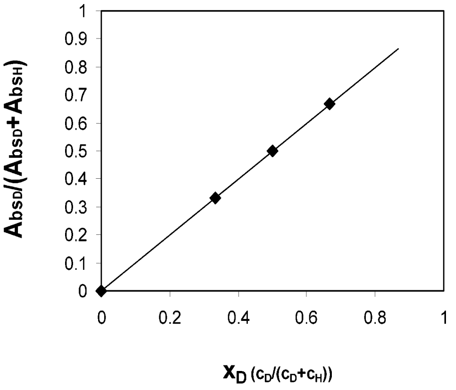
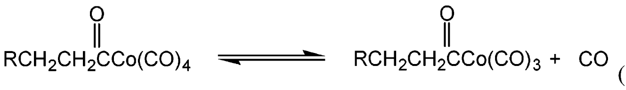


Figure 4. Plot of the "absorption fraction" of the deuterated aldehyde, i.e., the ratio between the 1714 cm^{-1} band and the sum of the 1736 and 1714 cm^{-1} bands, as a function of the mole fraction of the deuterated aldehyde with respect to the total aldehyde in the solution (x_D).

The slope of the line, R, shows that the extinction coefficient of the deuterated aldehyde at 1714 cm^{-1} is the same as that of the regular aldehyde at 1734 cm^{-1}.

3.2. Relationship between H_2/D_2 Molar Ratio in the Gas Phase and −CHO/−CDO Molar Ratio of the Products in Solution. The most important and most surprising result obtained in our studies of the Type II stoichiometric hydroformylation using mixtures of deuterium/hydrogen gas was the observation that the distribution of the aldehydic products, as far as the nature of the aldehydic H atom was concerned, depended on the composition of the gas mixture and not on the $HCo(CO)_4/DCo(CO)_4$ ratio in solution, as shown in Table 1. It appears that under the experimental conditions used, molecular hydrogen performs the hydrogenolysis of the acylcobalt carbonyl to give the aldehyde. Hence, similar to the mechanism observed in the Type I stoichiometric hydroformylation, the hydrogenolysis is initiated by the generation of a coordinatively unsaturated acyl complex, as shown below:



$$RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_4 \rightleftharpoons RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 + CO \quad (7)$$

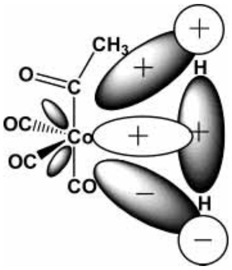


Figure 5. Schematic representation of the structure and bonding of the acylcobalt tricarbonyl complex with a coordinated hydrogen molecule.

TABLE 1: Summary of the Relative Amounts of $(CH_3)_3C(CH_2)_2CHO$ and $(CH_3)_3C(CH_2)_2CDO$ Obtained via the Type II Stoichiometric Hydroformylation with Various Initial $HCo(CO)_4/DCo(CO)_4$ Ratios and Different H_2/D_2 Ratios in the Gas Phase

%**H**Co(CO)$_4$	%**D**Co(CO)$_4$	% **H**$_2$	% **D**$_2$	% $RC(=O)\mathbf{H}$	% $RC(=O)\mathbf{D}$
68	32	100	0	100	0
93	7	50	50	50	50
63	37	0	100	0	100
8	92	50	50	50	50

It is not certain which cobalt orbital becomes vacant in the unsaturated complex, but it is likely that it is some *spd* hybrid orbital of the cobalt.[9,40] Such an empty orbital would permit complexation of molecular hydrogen through the filled bonding molecular orbital of the hydrogen molecule. The activation of the hydrogen molecule is then helped by the interaction of a filled *d* orbital of the metal with the antibonding σ^* orbital of hydrogen. The bonding in such a complex, shown in Figure 5, would be entirely analogous to that involved in metal−olefin π-bonding, and hence, a dihydrogen complex would constitute the precursor for the aldehyde formation.[41]

The experiments were conducted with initial equilibrated cobalt carbonyl solutions that contained different ratios of the regular and deuterated hydrides. The alkyl complexes formed in the first stage of olefin coordination would have incorporated the hydridic hydrogen, resulting in deuterium content that is commensurate to the amount of deuteride in solution, as shown below:

$$HCo(CO)_4 + (CH_3)_3C{-}CH{=}CH_2 \rightarrow (CH_3)_3C{-}CH_2{-}CH_2Co(CO)_4 \quad (8)$$

$$DCo(CO)_4 + (CH_3)_3C{-}CH{-}CH_2 \rightarrow (CH_3)_3C{-}CHD{-}CH_2Co(CO)_4 \quad (9)$$

These reactions are considered to be reversible and lead to isotopic scrambling. As a result, the alkyl formed has two different molecular weights, depending on the presence (or absence) of the deuterium atom in the hydrocarbon chain. This difference in molecular weight further translates through the subsequent acyl-formation stage and the hydrogen-activation stage. The ratio of the hydrocarbon moiety in the aldehyde containing hydrogen or deuterium atoms corresponds to the ratio of the hydride and deuteride cobalt complexes in the original equilibrated solution, while the ratio of the aldehydic hydrogen or deuterium corresponds to the ratio of the molecular hydrogen and deuterium in the gas phase. Mass spectra of the various

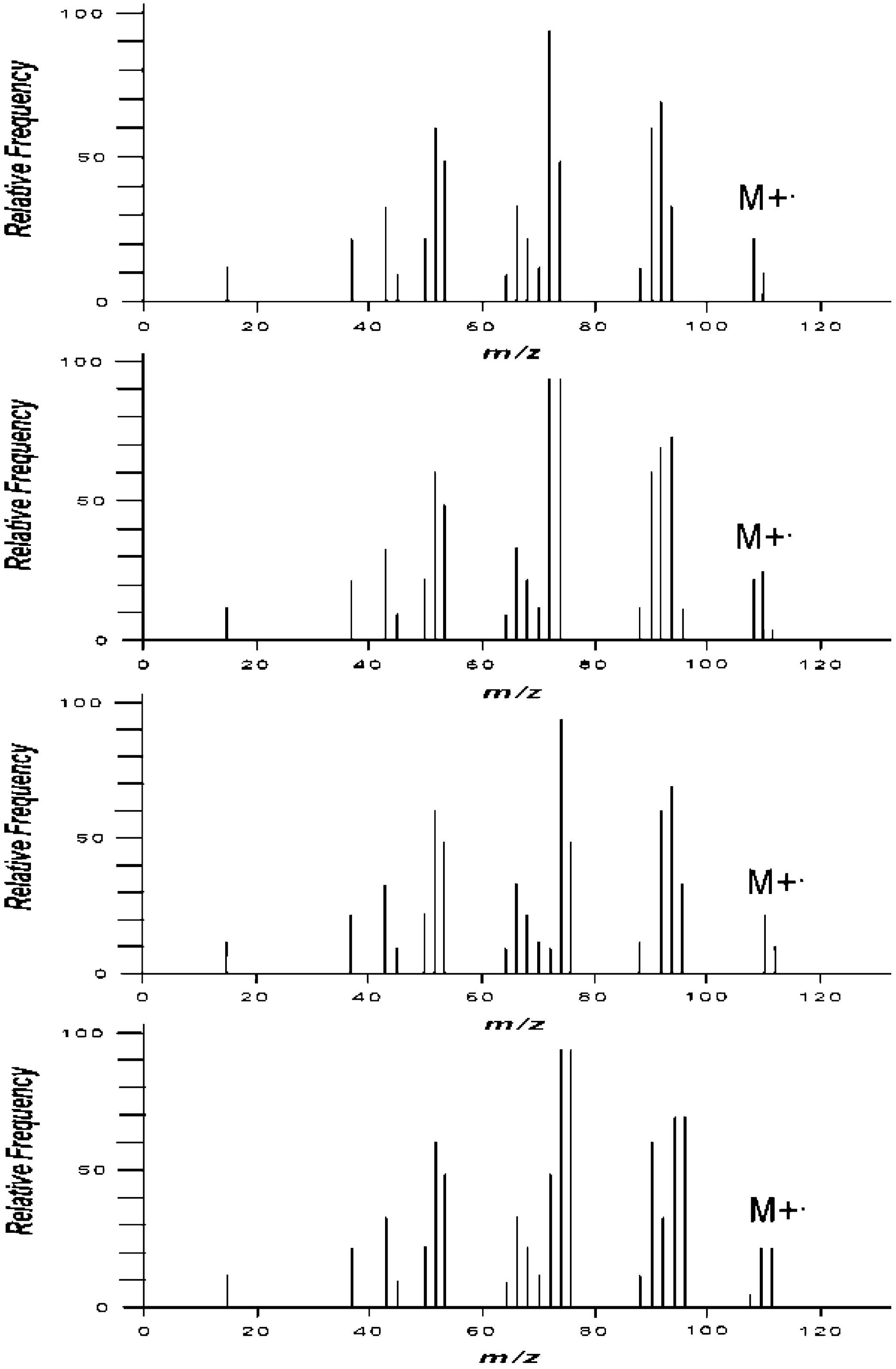


Figure 6. Mass spectra of the recovered aldehydic products resulting from the Type II stoichiometric hydroformylation reaction that were conducted with different initial $HCo(CO)_4$/$DCo(CO)_4$ ratios and different H_2/D_2 ratios in the gas phase. The sequence of the spectra exactly corresponds to the sequence in Table 2.

types of aldehydes formed with the Type II stoichiometric hydroformylation are shown in Figure 6 and summarized in Table 2. Clearly, the distribution of molecular masses of the products are consistent with the lack of correlation between the composition of the hydride species in solution and the composition of the gas phase. Moreover, exposure of preformed nondeuterated aldehyde, RC(O)H, and preformed deuterated aldehyde, RC(O)D, to D_2 and H_2, respectively, did not generate a detectable isotope exchange in the time frame that was commensurate with the actual duration of the hydroformylation reaction. This indicates that the two steps in the mechanism—the incorporation of the hydridic atom into the

TABLE 2: Summary of the Theoretical and Experimental Relative Abundance of the Molecular Ion Masses ($M^{\bullet+}$) of the Different Species Formed via the Type II Stoichiometric Hydroformylation with Various Initial $HCo(CO)_4$/$DCo(CO)_4$ Ratios and Different H_2/D_2 Ratios in the Gas Phase[a]

reaction conditions hydride/deuteride ratio and hydrogen/deuterium ratio	%R**H**CHO (MW = 114 g/mol) *m*/*z* = 114			%R**H**CDO + %R**D**CHO (MW = 115 g/mol) *m*/*z* = 115			%R**D**CDO (MW = 116 g/mol) *m*/*z* = 116		
	type I	expected	**actual**	type I	expected	actual	type I	expected	**actual**
$HCo(CO)_4$/$DCo(CO)_4$ **68:32** H_2/D_2 **100:0**	46.2	68	**69**	43.5	32	**31**	10.2	0	**0**
$HCo(CO)_4$/$DCo(CO)_4$ **93:7** H_2/D_2 **50:50**	86.5	46.5	**43**	13.0	50	**49**	0.5	3.5	**8**
$HCo(CO)_4$/$DCo(CO)_4$ **63:37** H_2/D_2 **0:100**	39.7	0	**0**	46.6	63	**66**	13.7	37	**34**
$HCo(CO)_4$/$DCo(CO)_4$ **8:92** H_2/D_2 **50:50**	0.6	4	**9**	14.7	50	**45**	84.6	46	**44**

[a] For comparison, the theoretical predictions of the relative abundance of the molecular ion masses ($M^{\bullet+}$) of the different species formed via the Type I stoichiometric hydroformylation are shown as well.

hydrocarbon chain and the hydrogenolysis of the acyl—are two independent processes involving two independent active intermediates and transition states, without any coupling effect between them.

4. Summary

In this article, we have shown that the stoichiometric hydroformylation reaction conducted in the presence of stoichiometric amounts of $HCo(CO)_4$ and CO (Type I) is not analogous to the stoichiometric hydroformylation reaction conducted in the presence of $Co_2(CO)_8$ and H_2 (Type II), as previously believed. The Type II reaction indeed proceeds via the formation of the hydride species, followed by the coordination of the olefin and its insertion into the M−H bond and the addition of a CO group, resulting in the formation of the acylcobalt complex, similar to the mechanism of the Type I reaction. But the similarity ends at this point. The presence of hydrogen in the gas phase in the Type II reaction drives the hydrogenolysis step to occur via a different pathway than that observed in the Type I reaction. While in the Type I reaction this step is carried out by a second molecule of $HCo(CO)_4$, in the Type II reaction this step is carried out by the hydrogen, as evidenced by the isotope effect in the aldehyde product distribution. The relative concentration of the deuterated aldehyde in the aldehydic product mixture corresponds precisely to the composition of D_2/H_2 in the gas phase and not to the composition of the hydride species in solution. These experiments, in conjunction with other studies,[41] provide strong evidence that the direct reaction of hydrogen or deuterium with the acyl complex intermediate (that is rapidly formed under stoichiometric conditions at low CO pressure) is not only a viable but rather the dominant reaction pathway for this type of stoichiometric hydroformylation reaction. These results were crucial in our re-interpretation of some of the fundamental aspects of the mechanism of the hydroformylation reaction and the various reactive cobalt carbonyl species involved in the reaction.[41]

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