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# The catalytic binuclear elimination reaction: Confirmation from in situ FTIR studies of homogeneous rhodium catalyzed hydroformylation

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ABSTRACT

In the past decade, considerable progress has been made in the understanding of catalytic systems which simultaneously possess both mononuclear and dinuclear intermediates. The present contribution begins by reviewing the necessary background concerning stoichiometric binuclear elimination. This is followed by a summary of in situ FTIR studies on corresponding homometallic and hetero-bimetallic catalytic binuclear eliminations. Pure component spectral estimates of the constituents present during the catalysis as well as their associated concentration profiles are used in order to model the rates of binuclear elimination during alkene hydroformations. The rates of product formation are linear–quadratic in metal loading for the homometallic case and linear–bilinear in the hetero-bimetallic case. Hetero-bimetallic catalytic binuclear elimination provides a well-defined mechanistic basis for synergism.

## 1. Introduction

Most homogeneous catalytic systems are believed to consist of catalytic cycles where all intermediates have one-and-the-same nuclearity. Indeed, a brief inspection of some of the standard texts confirms that most well-studies catalytic hydrogenations, catalytic hydroformylations, etc., are assumed to arise from catalytic cycles where each intermediate is mononuclear [1,2]. In the early 1960s, Heck and Breslow proposed the possible formation of organic products from the reaction of two mononuclear intermediates [3,4]. In the stoichiometric case, such a reaction would lead to the formation of an organic product and a binuclear complex. Subsequently, numerous studies were conducted on stoichiometric binuclear eliminations. Two distinct cases can be identified, namely, the homometallic case where both mononuclear organometallics are based on the same metal and the hetero-bimetallic case where the two mononuclear organometallic are based on different metals [4–25]. Extensive lists of known homogeneous homometallic and hetero-bimetallic stoichiometric binuclear eliminations are provided in Tables 1 and 2.

For completeness, it should be mentioned that a binuclear elimination is also believed to exist for a heterogenized homogeneous catalytic system [26]. Also, it can be noted that the well known bimetallic process for the carbonylation of methanol is not believed to be a catalytic binuclear elimination ($RML_n + R'ML_m \rightarrow RR' + M_2L_{n+m}$). Instead, it has been shown that the role of ruthenium is to abstract iodine from a iridium complex [27].

Over the past decade, a number of detailed in situ FTIR spectroscopic studies have been performed in order to identify systems which show rates of product formation consistent with the presence of a catalytic binuclear elimination reaction (CBER). Using alkene hydroformation as the model reaction, systems have been identified where (1) homometallic rhodium catalytic binuclear elimination exists as well as (2) hetero-bimetallic rhodium–manganese and rhodium–rhenium catalytic binuclear eliminations exist. In the present contribution, the in situ spectroscopic search for catalytic binuclear elimination is reviewed. A primary aim of this contribution is to increase the awareness within the homogeneous catalysis community that catalytic systems exist which simultaneously possess both mononuclear and dinuclear intermediates and that such systems have some unique characteristics which may prove attractive from a synthetic viewpoint.

## 2. Results and discussion

### 2.1. Homometallic CBER

Although Heck and Breslow introduced the very important observation that stoichiometric binuclear elimination exists (reaction 1, Table 1), it proved difficult to confirm the corresponding catalytic version. In the early 1980s, Mirbach used in situ FTIR to study the cobalt catalyzed reaction of 1-octene. In the latter

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**Table 1**
List of known homometallic stoichiometric binuclear elimination reactions.

| No | homometallic stoichiometric binuclear elimination reactions | Reference |
|---|---|---|
| 1 | $RCOCo(CO)_4 + HCo(CO)_4 \rightarrow Co_2(CO)_8 + RCHO$ | [4–6] |
| 2 | $2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2$ | [7,8] |
| 3 | $RCo(CO)_4 + HCo(CO)_4 \rightarrow Co_2(CO)_8 + RH$ | [9] |
| 4 | $2Os(CO)_4H_2 \rightarrow H_2Os_2(CO)_8 + H_2$ | [10–12] |
| 5 | $2Os(CO)_4(H)CH_3 \rightarrow HOs(CO)_4Os(CO)_4CH_3 + CH_4$ | [10–12] |
| 6 | $Os(CO)_4H_2 + Os(CO)_4(CH_3)_2 \rightarrow HOs(CO)_4Os(CO)_4CH_3 + CH_4$ | [10–12] |
| 7 | $Os(CO)_4H_2 + Os(CO)_4(H)CH_3 \rightarrow H_2Os_2(CO)_8 + CH_4$ | [10–12] |
| 8 | $2HMn(CO)_5 \rightarrow Mn_2(CO)_{10} + H_2$ | [13] |
| 9 | $(CO)_5MnR + HMn(CO)_5 \rightarrow \{Mn_2(CO)_9\} + RCHO$ | [14–16] |
| 10 | $2HRh(CO)_2(PPh_3)_2 \rightarrow Rh_2(CO)_2(PPh_3)_2 + H_2 + 2CO$ | [17] |
| 11 | $2HIr(CO)(PPh_3)_3 \rightarrow Ir_2(CO)_2(PPh_3)_4 + H_2 + 2PPh_3$ | [18] |
| 12 | $EtRe(CO)_5 + HRe(CO)_5 \rightarrow EtCHO + \{Re_2(CO)_9\}$ | [19] |
| 13 | $H^{-}Fe(CO)_4 + CH_3CH_2C({=}O)^{-}FePPh_3(CO)_3$ $\rightarrow CH_3CH_2CHO + \{Fe_2\ PPh_3\ (CO)_7\}$ | [20] |
| 14 | $(\eta^5\text{-}C_5H_5)Mo(CO)_3H + (\eta^5\text{-}C_5H_5)Mo(CO)_3R$ $\rightarrow \{(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5\} + RCHO$ | [21,22] |

study, the conclusion was reached that perhaps 4% of the product formation arises from CBER [28].

In the 1990s, our group reported a survey of in situ spectroscopic studies on the unmodified rhodium catalyzed hydroformation using different alkene substrates [29]. Most of the substrates provided very similar kinetic behaviors, and detailed studies of a few of these systems have shown that a classic unicyclic reaction mechanism consisting of mononuclear species is operating [30,31]. A few substrates, in particular cycohexene and cyclooctene, exhibited anomalous behavior. A detailed kinetic study using cyclohexene, which is a very slow substarte, showed that the rate of hydroformylation could be also accurately modeled using just a unicyclic rhodium mechanism alone [32].

However, in the case of cyclooctene as substrate, equilibrium controlled conversion of the precursor $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ was noted. Numerical analysis of the spectroscopic data provided good pure component spectra of the main organic and organometallic constituents present as well as their time dependent concentrations [33]. In addition, the presence of a rather significant $HRh(CO)_4$ concentration was also confirmed. The final expression for aldhyde formation included two terms. The first term involved just one organmetallic $RCORh(CO)_4$ and the second involved the product of two organometallics, namely, $RCORh(CO)_4$ and $HRh(CO)_4$ (Eq. (1)). Such an expression, which is linear–quadratic in metal, is particularly interesting from a metal utilization view.

$$\text{rate} = k_1[RCORh(CO)_4] + k_2[RCORh(CO)_4][HRh(CO)_4] \tag{1}$$

**Table 2**
List of known bimetallic stoichiometric binuclear elimination reactions.

| No | bimetallic stoichiometric binuclear elimination reactions | Reference |
|---|---|---|
| 1 | $EtRe(CO)_5 + HMn(CO)_5 \rightarrow EtCHO + \{Re(CO)_4Mn(CO)_5\}$ | [19] |
| 2 | $(\eta^5\text{-}C_5H_5)ReH + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)(H)$ $Re(\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4 + CO + CH_4$ | [23] |
| 3 | $EtRe(CO)_5 + HW(CO)_3Cp \rightarrow CH_3CH_3 + Re(CO)_5W(CO)_3Cp$ | [19] |
| 4 | $HRe(CO)_5 + Os(CO)_4(H)CH_3 \rightarrow HOs(CO)_4Re(CO)_5 + CH_4$ | [11] |
| 5 | $HCo(CO)_4 + EtOC(O)Mn(CO)_5 \rightarrow EtOC(O)H + MnCo(CO)_9$ | [24] |
| 6 | $HCo(CO)_4 + EtOC(O)CH_2Mn(CO)_5 \rightarrow EtOC(O)CH_3 + MnCo(CO)_9$ | [24] |
| 7 | $HMn(CO)_5 + CH_3AuPPh_3 \rightarrow Au(PPh_3)Mn(CO)_5 + CH_4$ | [25] |
| 9 | $HMn(CO)_5 + EtOC(O)Co(CO)_4 \rightarrow EtOCHO + MnCo(CO)_9$ | [24] |
| 9 | $HMn(CO)_5 + EtOC(O)CH_2Co(CO)_4 \rightarrow EtOC(O)CH_3 + MnCo(CO)_9$ | [24] |
| 10 | $(\eta^5\text{-}C_5H_5)_2MoH_2 + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)$ $(CO)Mo(\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4 + H_2 + CH_4$ | [23] |
| 11 | $(\eta^5\text{-}C_5H_5)_2WH_2 + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)(CO)$ $W(\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4 + H_2 + CH_4$ | [23] |
| 12 | $HOs(CO)_4Si(CH_3)_3 + CH_3AuPPh_3 \rightarrow Au(PPh_3)$ $Os(CO)_4Si(CH_3)_3 + CH_4$ | [25] |
| 13 | $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2 + (\eta^5\text{-}C_5H_5)Mo(CO)_3H$ $\rightarrow (\eta^5\text{-}C_5H_5)_2CH_3ZrMo(\eta^5\text{-}C_5H_5)(CO)_3 + CH_4$ | [26] |

Although the presence of a homometallic dinuclear species, particular $Rh_2(CO)_8$ could not be confirmed spectroscopically, the two term expression (Eq. (1)) strongly suggested that binuclear elimination was taking place. Indeed, at the mean reaction conditions used in that study, the second term (involving the product $[RCORh(CO)_4][HRh(CO)_4]$) accounted for circa 40% of the product aldehyde formation. Taken together, the spectroscopic and kinetic results suggested two simultaneous catalytic mechanisms for aldehyde formation, namely, (1) a unicyclic system of mononuclear rhodium intermediates and (2) a CBER involving the crucial reaction of $RCORh(CO)_4$ and $HRh(CO)_4$. The proposed interconnected system is shown in Fig. 1.

### 2.2. Hetero-bimetallic CBER

Detailed spectroscopic studies were performed on rhodium catalyzed hydroformylations starting with $Rh_4(CO)_{12}$ and a mixture of $HMn(CO)_5/Mn_2(CO)_{10}$ as catalytic precursors, and both 3,3 dimethylbut-1-ene and cyclopentene were used as substrates in the hydroformation reaction [34–36]. Numerical analyses of the spectroscopic data provided good pure component spectra for the main organic and organometallic constituents present ($Rh_4(CO)_{12}$, $RCORh(CO)_4$, $HMn(CO)_5$, $Mn_2(CO)_{10}$) as well as their time dependent concentrations. The final expression for aldhyde formation included two terms. The first involved just one organometallic $RCORh(CO)_4$ and the second involved the product of two organometallics $RCORh(CO)_4$ and $HMn(CO)_5$ (Eq. (2)). Such an expression, which is linear–bilinear in metal, provides a clear mechanistic basis for synergistic effects in this Rh–Mn system.

$$\text{rate} = k_1[RCORh(CO)_4] + k_2[RCORh(CO)_4][HMn(CO)_5] \tag{2}$$

Although the presence of a hetero-bimetallic dinuclear species, particular $RhMn(CO)_9$ could not be confirmed spectroscopically, the two term expression (Eq. (2)) strongly suggested that binuclear elimination was taking place. Indeed, at the mean reaction conditions used in that study, the second term (involving the product $[RCORh(CO)_4][HMn(CO)_4]$) accounted for circa 60% of the product aldehyde formation. Taken together, the spectroscopic and kinetic results suggested two simultaneous catalytic mechanisms for aldehyde formation, namely, (1) a unicyclic system of mononuclear rhodium intermediates and (2) a CBER involving the crucial reaction of $RCORh(CO)_4$ and $HMn(CO)_5$. The proposed interconnected system is shown in Fig. 2.

Detailed spectroscopic studies were also performed on rhodium catalyzed hydroformylations starting with $Rh_4(CO)_{12}$ and $HRe(CO)_5$ as catalytic precursors, and both 3,3 dimethylbut-1-ene and cyclopentene were used as substrates in the hydroformation reaction [36,37]. Numerical analysis of the spectroscopic data provided good pure component spectra of the main organic and organometallic constituents present ($Rh_4(CO)_{12}$, $RCORh(CO)_4$, $HRe(CO)_5$, $RhRe(CO)_9$) as well as their time dependent concentrations. The final expression for aldhyde formation included two terms. The first involved just the $RCORh(CO)_4$ and the second involved the product of $RCORh(CO)_4$ and $HRe(CO)_5$ (Eq. (3)). Again, such an expression, which is linear–bilinear in metal, provides a clear mechanistic basis for synergistic effects in this Rh–Re system.

$$\text{rate} = k_1[RCORh(CO)_4] + k_2[RCORh(CO)_4][HRe(CO)_5] \tag{3}$$

In contrast to the Rh–Mn system, the mixed Rh–Re system provided the very important spectroscopic observation of a hetero-bimetallic dinuclear species $RhRe(CO)_9$. In addition, it provided the very important kinetic result that hydrogen activation on $RhRe(CO)_9$ is very rapid. In the final analysis, it was demonstrated that the rate of product formation (involving the product $[RCORh(CO)_4][HRe(CO)_5]$) was exactly equal to the rate of

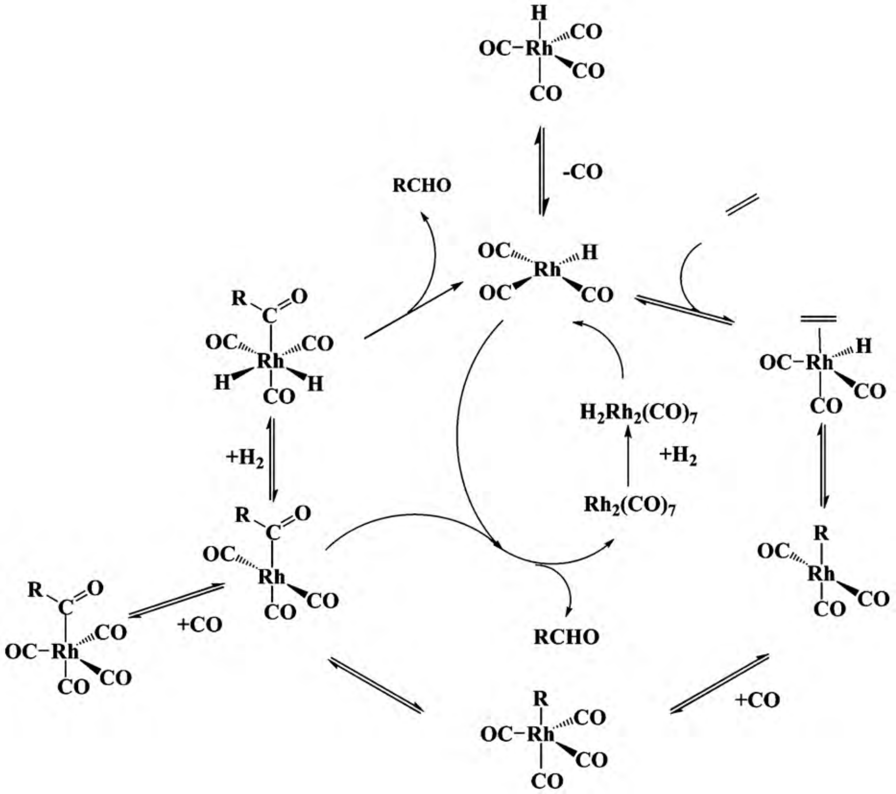

**Fig. 1.** The proposed reaction mechanism for the simultaneous interconnected unicyclic Rh cycle and homometallic Rh–Rh CBER.

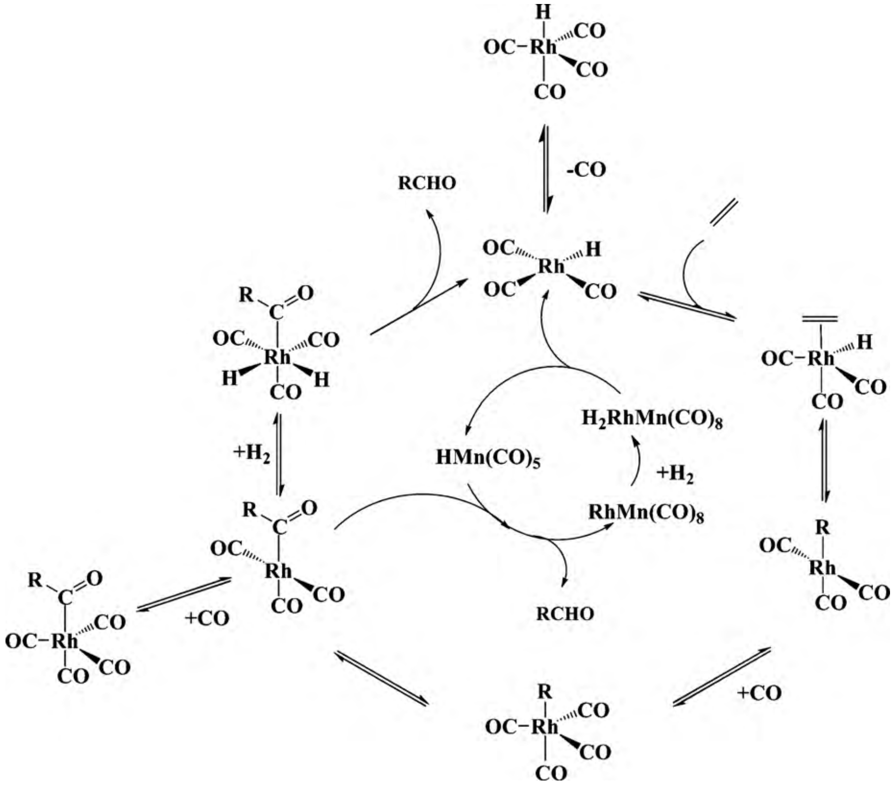

**Fig. 2.** The proposed reaction mechanism for the simultaneous interconnected unicyclic Rh cycle and bimetallic Rh–Mn CBER.

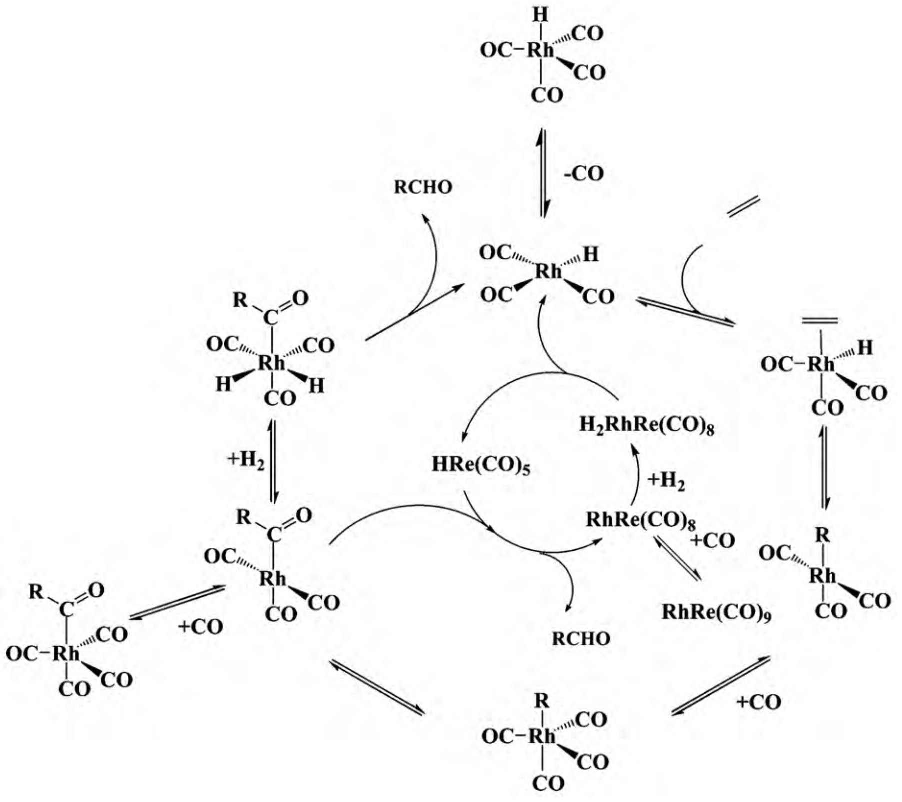

**Fig. 3.** The proposed reaction mechanism for the simultaneous interconnected unicyclic Rh cycle and bimetallic Rh–Re CBER.

hydrogen activation on $RhRe(CO)_9$. At the mean reaction conditions used in this study, the term involving the product $[RCORh(CO)_4][HRe(CO)_5]$ was responsible for circa 80% of the product aldehyde formation. Thus the mixed Rh–Re system clearly showed that there are two simultaneous catalytic mechanisms for aldehyde formation, namely, (1) a unicyclic system of mononuclear rhodium intermediates and (2) a CBER involving the crucial reaction of $RCORh(CO)_4$ and $HRe(CO)_5$. The proposed interconnected system is shown in Fig. 3.

## 3. Experimental

### 3.1. General procedure

The experiments were performed with puriss 3,3 dimethylbut-1-ene or cyclopentene or cyclooctene (99.9%, Fluka), carbon monoxide (99.97%, Saxol), hydrogen (99.999%, Saxol), $Rh_4(CO)_{12}$ (98% Strem), $HRe(CO)_5$ (99%, Strem) and puriss *n*-hexane (99.6%, Fluka). $HMn(CO)_5$ was prepared using a modification of a known literature preparation [35]. The alkene, gases and solvent were extensively purified prior to use according to previously used procedures [35], and all solution preparations and transfers were made under Schlenk techniques[38].

All hydroformylation experiments were performed in a closed batch reactor (1.5 L stainless steel autoclave, Buchi–Uster, Swizerland or a in-house constructed 100 ml stainless steel reactor) system. A recycle loop circulated the liquid phase from the reactor, through a high pressure hermetically sealed pump, and a high pressure FTIR cell (with 15 mm thick $CaF_2$ windows), and then back to the reactor. All spectra were measured on a Perkin Elmer System 2000 FTIR or a Bruker Vertex 70 with resolution 4 $cm^{-1}$. Details of the experimental setup and a schematic diagram can be found elsewhere [30,39].

For each of the above mentioned CBER systems (Rh–Rh, Rh–Mn, Rh–Re), circa 20 batch experiments were performed. In each set of experiments, one experimental parameter was systematically varied while the remaining variables were held essentially constant. The detailed experimental design involved various loadings of alkene, main precursor $Rh_4(CO)_{12}$, second metal $HRe(CO)_5$ or $HMn(CO)_5$, partial pressure of $H_2$ and CO, and temperature.

### 3.2. Numerical analysis

Circa 1000 in situ FTIR spectra were collected for each of the above mentioned CBER experimental studies. These FTIR spectra covered the interval 1550–2500 $cm^{-1}$ with data intervals of

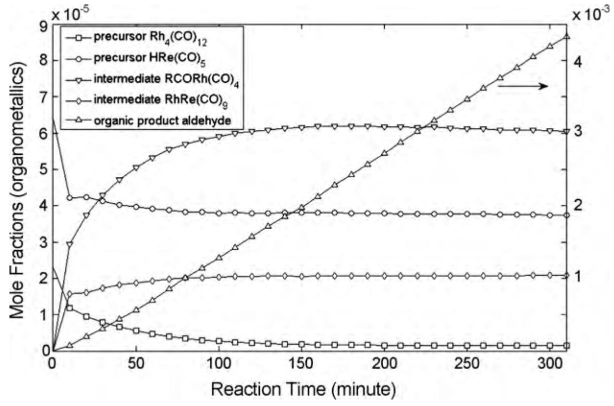

**Fig. 4.** A typical concentration profiles for both organic and organometallic species, from one of the batch experimental runs, in the Rh–Re bimetallic catalyzed hydroformylations.

0.2 $cm^{-1}$. The in situ FTIR spectra were then consolidated and analysed with the spectral reconstruction algorithm Band–Target Entropy Minimization (BTEM)[40,41] in order to recover the pure component spectra present. Then a set of algebraic system identification algorithms were used to determine the absorptivities of the organic and organometallic species present as well as their moles and mole fractions[42]. A typical set of concentration profiles for both organic and organometallic species is shown in Fig. 4. The solvent n-hexane was used as an internal standard, and its absorptivity was measured independently. BTEM has been successfully used to analyze data from numerous homogeneously catalyzed reactions. A review of this approach and its application to homogeneous catalysis can be found elsewhere [43].

## 4. Conclusions

As this review documents, in situ FTIR spectroscopic studies were crucial in providing the needed spectroscopic and kinetic evidence to support the existence of a CBER mechanism in a few specific cases of alkene hydroformylation. The activity of the systems studied were in fact the sum of contributions from both unicyclic and CBER mechanisms. The homometallic and heterobimetallic cases provide distinctly different kinetic expression which have relevance to metal utilization and provide a phenomenological basis for synergism.

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