ELSEVIER

Journal of Molecular Catalysis A: Chemical 103 (1995) 11–16

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Towards catalytic selective dimerisation of olefins or reaction related to hydroformylation? $Co_2(CO)_8$ versus $RhCl(PPh_3)_3$

Marc A. Fontaine *, Rino Messere, Alfred F. Noels

Centre of Education and Research on Macromolecules (C.E.R.M), Institute of Chemistry (B.6), University of Liège, B-4000 Liège, Belgium

Received 20 January 1995; accepted 9 May 1995

Abstract

Dicobaltoctacarbonyl, $Co_2(CO)_8$, in pyridine and under syngas pressure, catalyses the direct and selective dimerisation of aromatic olefins to the corresponding saturated hydrocarbons. Under similar conditions, chlorotris(triphenyl)phosphine rhodium, $RhCl(PPh_3)_3$, promotes the selective reductive coupling of intermediate aldehydes C_{n+1} (resulting of an initial hydroformylation of the starting olefins C_n) into new saturated monoaldehydes C_{2n+2}. The outcome of these reactions is markedly influenced by the reaction conditions and by the structure of the starting olefins. Pyridine is essential as a solvent. A tentative mechanistic proposal is discussed for both reactions.

Keywords: Olefins; Styrene; Hex-1-ene; Coupling reaction; Hydroformylation; Pyridine; Rhodium; Dicobaltoctacarbonyl; Syngas

1. Introduction

Dicobaltoctacarbonyl and chlorotris(triphenyl)phosphine rhodium, Wilkinson's catalyst, are used as homogeneous catalysts (or catalyst precursors) in one of the most important industrial process, the olefin hydroformylation reaction [1]. Although this reaction is usually carried out in aromatic or chlorinated aliphatic solvents such as, benzene, toluene, 1,2-dichloroethane, ..., or even in neat olefin substrates, some systems are also reported where pyridine is added as a promoter [2,3].

We have recently described the dramatic modification of the reaction selectivity in the coupling reactions of aldehydes with $Co_2(CO)_8$ [4] or $RhCl(PPh_3)_3$ [5] as catalysts under a pressure of syngas in pyridine as a solvent. C_{2n-1} symmetrical ketones or saturated C_{2n} aldehydes are then produced, respectively with cobalt- or rhodium-based systems [5,6] (Fig. 1).

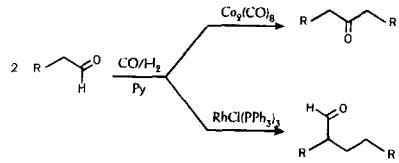

Fig. 1. Selective coupling of aldehydes to give symmetrical ketones or monosaturated aldehydes: $Co_2(CO)_8$ versus $RhCl(PPh_3)_3$.

Considering the reaction conditions for which the coupling reactions of aldehydes were observed, it seemed opportune to test olefins as substrates, as they are potential precursors of aldehydes under syngas. Provided the hydroformylation reaction can satisfactorily be carried out in pyridine, the reaction sketched in Fig. 1 could pave the way to a one-pot synthesis of dimer

* Corresponding author. Fax (+32-41)663497

SSDI 1381-1169(95)00098-4

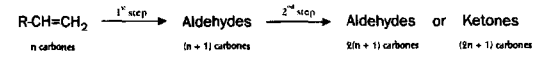

Fig. 2. Schematic one-pot synthesis of C_{2n+1} ketones and C_{2n+2} aldehydes from C_n olefins.

ketones or aldehydes directly from the olefins according to Fig. 2.

The outcome of the reaction with the two catalytic systems proved to be quite different. Herein we report the results obtained with both systems.

2. Experimental

2.1. Typical procedure for the dicobaltoctacarbonyl-based coupling reaction

Olefin (20 mmol) and $Co_2(CO)_8$ (0.96 mmol) were dissolved in dry pyridine (10 ml) in a Pyrex jacketed stainless-steel autoclave. The system was then closed and purged once with carbon monoxide. 10 MPa of synthesis gas (ratio $CO:H_2 = 8:2$) was then introduced and the mixture heated for 12 h at 140°C. After cooling down and venting the autoclave, the solution was analysed by gas chromatography.

2.2. Typical procedure for the chlorotris(triphenyl)phosphine rhodium-based coupling reaction

Olefin (20 mmol) and $RhCl(PPh_3)_3$ (6.5×10^{-2} mmol) were dissolved in dry pyridine (10 ml). This homogeneous solution was rapidly charged in a Pyrex jacketed stainless-steel autoclave, then pressurised to 11 MPa of syngas (ratio $CO:H_2 = 9:2$) and heated to 160°C for 12 h. After cooling down and degassing, the homogeneous solution was kept under nitrogen and aliquots were removed for analysis.

Yields were calculated by GC with dibenzyl as an internal standard, after calibration and introduction of substance-specific correction factors for the most important products, as described in [5].

Products were identified by comparison of their retention times on at least two different GC capillary columns and spectroscopically by coupled GC–FTIR and GC–MS.

Gas-chromatographic analyses were performed with a Perkin Elmer Model 8500 gas chromatograph using two different fused silica capillary columns (FID with nitrogen as carrier gas): a 30 m × 0.53 mm WCOT, CP-Sil8-CB column (Chrompack) and a 30 m × 0.32 mm WCOT, FFAP-CB column (RSL).

3. Results and discussion

3.1. $Co_2(CO)_8$ based system

Cobalt carbonyls promote a variety of carbonylation reactions such as hydroxy- or alkoxycarbonylation [7], amido-carbonylation [8] or of course, hydroformylation [1], etc. Our research was aimed at checking the feasibility of a direct access to symmetrical ketones from aldehydes resulting of an in situ olefin hydroformylation. The outcome of the reaction of styrene and some of its derivatives are however rather surprising (a preliminary account of this part of work has already been published [9]). The expected symmetrical ketone was not obtained and products resulting from hydroformylation reactions **5**, **6**, **9** and **10** were formed only in very small amount (total yield $< 1\%$). Instead, the main reaction resulted from a reductive dimerisation of the olefin, i.e. 1,3-diphenylbutane **2** (yield 43%) and from a hydrogenation of the starting olefin, i.e. ethylbenzene (yield 25%). Other hydrocarbons mostly dimers **4**, **7**, **8** and saturated trimers were also formed in small amounts as indicated in Fig. 3. Unidentified heavier products resulting from multiple condensations account for the balance of the reaction.

The reaction was extended to some styrene derivatives [9] and to some aliphatic olefins. No coupling products were observed with hex-1-ene but vinylcyclohexane or 4-vinylcyclohexene gave modest yield of the corresponding dimers (Fig. 4).

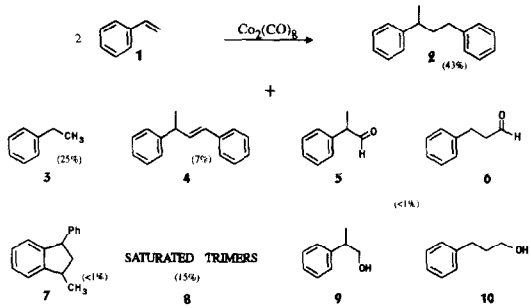

Fig. 3. Dimerisation of styrene 1 catalysed by $Co_2(CO)_8$ in pyridine.

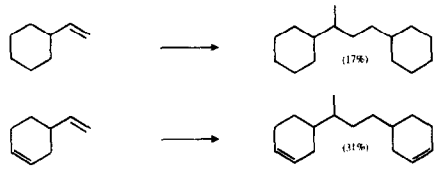

Fig. 4. Dimerisation of vinylcyclohexane and 4-vinylcyclohexene.

Table 1
Comparison between the system used by us (dimerisation) and the system described by Botteghi (hydroformylation); in both cases $Co_2(CO)_8$ is the catalyst, and styrene the substrate

Parameters	Dimerisation (our system)	Hydroformylation (Botteghi's system)
pyridine	solvent	promoter
temperature (°C)	140	60–120
total pressure MPa	10	8
CO:H_2 ratio	4:1	1:1

It is interesting to compare our system where the reaction is carried out in neat pyridine with that described by Botteghi and co-workers where pyridine is utilised as a promoter (ratio 1:1 with cobalt) in benzene as a solvent [2]. Under relatively similar reaction conditions, on the one hand styrene is hydroformylated and on the other hand (this work), reductively dimerized. The main experimental characteristics of both systems are summarised in Table 1.

We have carried out a run for which the experimental conditions are very close to those described by Botteghi ($CO/H_2 = 1$; $P_T = 10$ MPa; $T = 140$°C), excepted for the relative amount of pyridine. The results are then the following: 12% of **2**, 15% of **3** and 11% of **8**. Traces ($< 1\%$) of hydroformylation compounds and **4** were also detected. In this case, the proportion of heavier products is more important. Although gas composition could also contribute to the reaction selectivity, it seems that the key difference comes from the solvent. Some authors suggest that the role of pyridine is mainly to promote the formation of the active hydridocobaltcarbonyl complexes [10]. Botteghi goes further and postulates that pyridine influences the rate of oxidative addition of hydrogen to intermediate acyl- and/or alkylcobalt complexes and their subsequent reductive elimination. Indeed, in Botteghi's case, the aldehyde distribution was not affected by the presence or not of pyridine. In our case, the role of pyridine is probably to promote the formation of hydridocobaltcarbonyl species in which one or several carbon monoxide ligands are substituted by pyridine. The different stereoelectronic properties of the new complexes would then favour dimerisations.

$$3\,Co_2(CO)_8 + 12\,Py \rightleftarrows 2\,[CoPy_6]^{2+}[Co(CO)_4]_2^- + 8\,CO$$

Fig. 5. Basic reaction between pyridine (Py) and dicobaltoctacarbonyl.

The cobalt carbonyls disproportionation reaction promoted by pyridine to give the homonuclear ionic pair (HNIP), $[CoPy_6]^{2+}[Co(CO)_4]_2^-$ is relatively well documented in the literature [11,12] (Fig. 5). Blank experiments in various solvents again [9] stressed the importance of pyridine utilised as a solvent.

The infrared spectrum of our starting solution showed a single broad band at 1888 cm^{-1} which is attributed to the anion $Co(CO)_4^-$. This single absorption band indicates the tetrahedral structure of this anion. It is known that the formation of this ionic pair is influenced by the pressure in CO and/or H_2. Indeed, Markó has shown that the formation of HNIP is inhibited by high pressure of CO [12], whereas Buller has described in a study of the hydrocarboxylation of butadiene that the system evolves toward the formation of a monopyridine-containing complex, $HCo(CO)_3Py$ (Fig. 6) [13].

$$[CoPy_6]^{2+}[Co(CO)_4]_2^- \overset{CO}{\rightleftarrows} [Co_2(CO)_6Py_2] \rightleftarrows [Co(CO)_3Py]_2$$
$$[Co(CO)_3Py]_2 \overset{H_2}{\rightleftarrows} 2\,HCo(CO)_3Py$$

Fig. 6. Evolution of the HNIP in the simultaneous presence of CO and H_2.

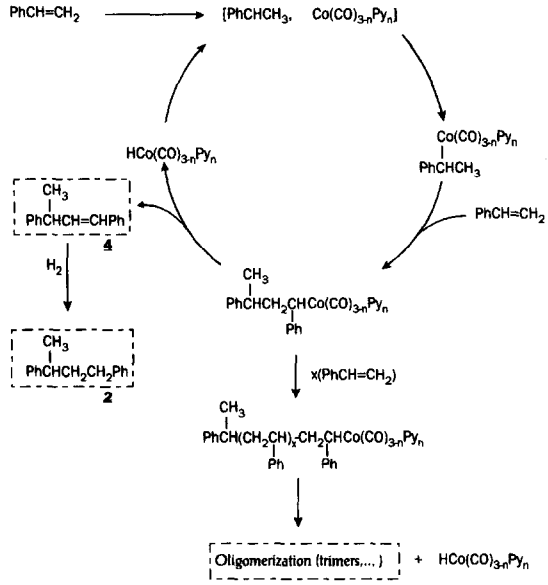

Fig. 7. Mechanistic proposal for the dimerisation of styrene and its derivatives.

A complex of the type $HCo(Py)_n(CO)_m$, $m+n=4$, could be the catalytically active species responsible for the olefin dimerisation.

In agreement with our experimental results and the literature data, we can propose the following mechanism for the styrene dimerisation (Fig. 7).

The essential feature of this cycle is the presence of a radical pair like $[PhCH^{\cdot}CH_3, {}^{\cdot}Co(CO)_{3-n}Py_n]$. Why a radical pathway? First, addition to the system of radical scavengers such as CCl_4, TEMPO, ..., totally inhibits the reaction. The homolytic rupture of the cobalt–carbon bond and the existence of radical pairs are amply documented. They were unambiguously characterised by Orchin and Pattenden [14]. Kinetic results also support the existence of such pairs in the hydrogenation of styrene by $HCo(CO)_4$ as well as in the formation of acylcobalt tetracarbonyls under CO [15]. Markó et al. have also demonstrated that 1,3-diphenylbutane **2** is produced as by-products (10%) during the hydroformylation of styrene catalysed by carbonyl complexes of iron [16]. They considered this observation as a proof of a radical mechanism.

The following steps of our proposal are more classical: insertion of a second molecule of styrene followed by β-H elimination to give the 1,3-diphenylbut-1-ene **4** that is finally hydrogenated to 1,3-diphenylbutane **2**. This last step has been confirmed by the fact that **4** is the only product (>30%) when the reaction is carried out under a pressure of pure carbon monoxide (no hydrogen present).

3.2. *$RhCl(PPh_3)_3$ based system*

When the reaction is carried out in pyridine with Wilkinson's catalyst instead of dicobaltoctacarbonyl, olefin hydroformylation occurs as the first reaction. Indeed, styrene is then hydroformylated into α-methylphenylacetaldehyde (86%) and 3-phenylpropionaldehyde (8%). Small amounts of the two dimer aldehydes, 2-benzyl-5-phenylpentanal **11** and 2-methyl-2,4-diphenylpentanal **12**, resulting of the homo-coupling reaction of **5** and **6** (Fig. 8) are also observed. In fact, as the α-phenylalkylrhodium is relatively more stable than its linear isomer [1,17], the branched aldehyde is mainly produced, which prevents further coupling reaction to dimer aldehyde. We have indeed shown that coupling is not observed with α-substituted aldehydes [5]. In order to gain further insight into the reaction mechanism we tested the hex-1-ene as model of a linear aliphatic olefin.

Hydroformylation of hex-1-ene **13** leads to a higher ratio of linear aldehyde. Besides heptanal **14** and 2-methylhexanal **15**, the two expected

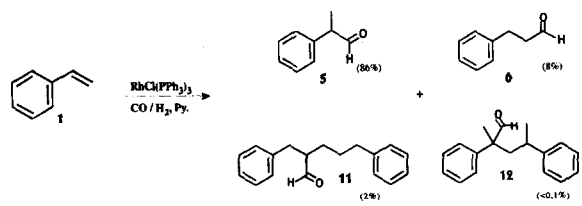

Fig. 8. In neat pyridine, styrene **1** gives mainly the aldehydes **5** and **6** which come from the hydroformylation of **1**. Only traces of aldehydes **11** and **12** resulting of the coupling reaction are observed.

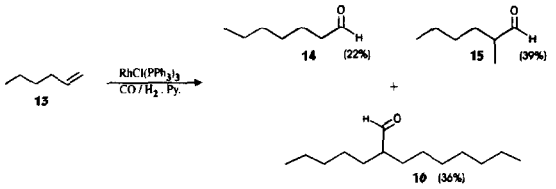

Fig. 9. Hydroformylation-coupling reaction with hex-1-ene as olefin (same experimental conditions as Fig. 8).

aldehydes resulting of the hydroformylation reaction, a sizeable amount of the 2-*n*-pentylnonanal **16** is also formed (36% yield) (Fig. 9).

The influence of amines as modifying ligands in hydroformylation reactions catalysed by rhodium complexes is known for more than 20 years [18]. The precise role of the amine has not been elucidated in most cases. Kiji et al. showed in 1985 that the activity of $RhCl(CO)PPh_3$ for catalysing the hydroformylation of formaldehyde is greatly enhanced in pyridine [19]. It was also later reported that rhodium-catalysed olefin hydroformylation was slow in the presence of excess pyridine [20]. More recently, aldehydes (n+iso) were synthesised in 80% yield by using $Rh(acac)[P(OPh)_3]_2$/pyridine (1:0.6) catalytic system. The active species did apparently not bind pyridine as a ligand [3] but it was proposed that the role of pyridine rather was to promote the formation of the active species, $HRh(CO)[P(OPh)_3]_3$.

We have started, in collaboration with Heaton's group, a HP-NMR study concerning the fate of the Wilkinson's catalyst in pyridine [21]. It was found that under a pressure of carbon monoxide and hydrogen. The starting Wilkinson's complex was completely converted. The predominant species was a cationic species *cis*-$[Rh(py)_2(PPh_3)_2]Cl$. This cation was no longer present after the aldehyde coupling reaction. All the new species have however not yet been fully characterised.

There is thus ample evidence that the addition of pyridine (in quasi equimolar amount or in large excess) has a dramatic influence on the structure of the initial catalyst complex and thus on the outcome of the reaction.

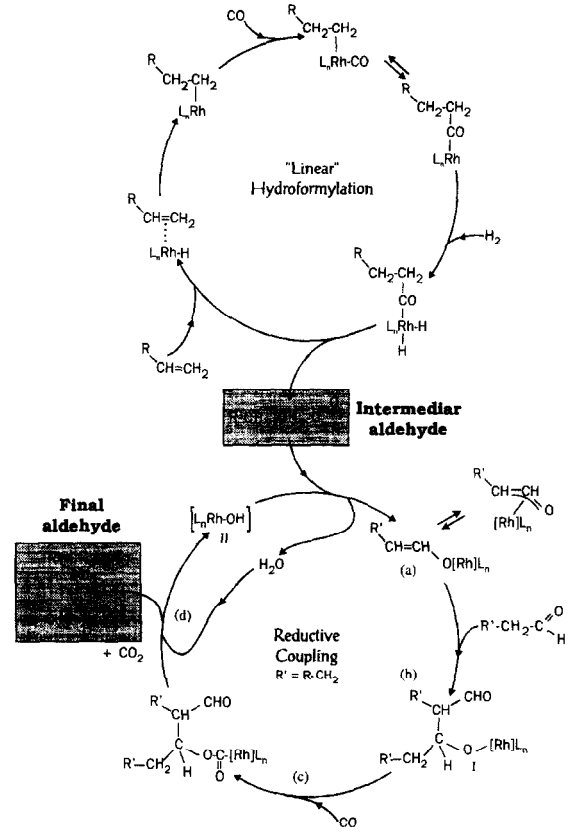

Fig. 10. Mechanistic proposal for the rhodium-based catalytic system.

We have summarised in the Fig. 10, a tentative mechanistic proposal which accounts for most of the observed facts. The first cycle includes the classical oxo mechanism yielding the linear isomer [22]. The second cycle is related to the preliminary observations made for the direct couplings of aldehydes and commented on in [5]. This latter cycle can roughly be split into four main steps: (a) formation of an enol followed by (b) reaction with another aldehyde to give an alkoxyrhodium complex (**I**); (c) 'insertion' of the carbon monoxide into the metal–alkoxy group, (d) elimination of the dimer aldehyde (by hydrolysis or protonolysis) yielding a rhodium–hydroxy complex (**II**) [5], possibly the real active species.

4. Conclusions

$Co_2(CO)_8$ and $RhCl(PPh_3)_3$ display quite different behaviours in the presence of olefins under

syngas. The cobalt based complex promotes the coupling reactions of aromatic olefins into the corresponding (branched) saturated hydrocarbons. Two reaction pathways are operative with Wilkinson's catalyst: on the one hand formation of aldehydes via a 'classical' hydroformylation reaction and on the other hand dimerization of these aldehydes as described in [5] and [6]. The outcome of the reaction strongly depends upon the presence of pyridine as a solvent. Ongoing efforts are directed towards a more precise study of the active species and towards synthetic applications in aliphatic chemistry.

Acknowledgements

We thank Professor A.J. Hubert (Liège) for his interest in this work and the 'National Fund for Scientific Research' (F.N.R.S.), Belgium, for the purchase of major instrumentation.

References

[1] (a) T. Ziegler and L. Versluis, in W.R. Moser and D.W. Slocum (Eds.), Homogeneous Transition Metal Catalyzed Reactions, Advances in Chemistry Series, Vol. 230, American Chemical Society, Washington, DC, 1992, p. 75, and references cited therein; (b) A. Oswald, D. Hendriksen, R. Kastrup and E. Mozeleski, in W.R. Moser and D.W. Slocum, (Eds.), Homogeneous Transition Metal Catalyzed Reactions, Advances in Chemistry Series, Vol. 230, American Chemical Society, Washington, DC, 1992, p. 395, and references cited therein; (c) G. Parshall and S. Ittel, Homogeneous Catalysis Wiley-Interscience, New York, 1992.

[2] (a) C. Botteghi, M. Branca, M. Marchetti and A. Saba, J. Organomet. Chem., 161 (1978) 197; (b) C. Botteghi, S. Paganelli, L. Bigini and M. Marchetti, J. Mol. Catal., 93 (1994) 279.

[3] A.M. Trzeciak, J. Organomet. Chem., 390 (1990) 105.

[4] M. Fontaine, A.F. Noels, A. Demonceau and A.J. Hubert, Tetrahedron Lett., 31 (1990) 3117.

[5] A.F. Noels, R. Messere, M. Fontaine and A. Demonceau, J. Catal., 147 (1994) 107.

[6] M. Fontaine, A. Demonceau, R. Messere, A.F. Noels, E. Peris and P. Lahuerta, J. Mol. Catal. A, 96 (1995) 107.

[7] H. Alper, Fund. Res. Homogeneous Catal., 4 (1984) 79.

[8] (a) M. Wakamatsu, J. Uda and N. Yamakami, J. Chem. Soc., Chem. Commun., (1971) 1540; (b) J.J. Lin and J.F. Knifton, in W.R. Moser and D.W. Slocum, (Eds.), Homogeneous Transition Metal Catalyzed Reactions, Advances in Chemistry Series, Vol. 230, American Chemical Society, Washington, DC, 1992, p. 235, and references cited therein.

[9] M. Fontaine, A.J. Hubert, A.F. Noels, A. Demonceau and P. Teyssié, J. Organomet. Chem., 417 (1991) C28.

[10] (a) R. Iwanaga, Bull. Chem. Soc. Jpn., 35 (1962) 865; (b) L. Roos and M. Orchin, J. Org. Chem., 31 (1966) 3015.

[11] (a) W. Hieber, Adv. Organomet. Chem., 8 (1970) 1; (b) G. Fachinetti, G. Fucki and T. Funaioli, J. Org. Chem., 301 (1986) 91.

[12] A. Sisak and L. Markó, J. Organomet. Chem., 330 (1987) 201.

[13] U. Buller, Dissertation, RWTH, Aachen (Germany), 1980.

[14] (a) T. Nalesnik and M. Orchin, Organometallics, 1 (1982) 223; (b) G. Pattenden, Chem. Soc. Rev., 17 (1988) 361.

[15] F. Ungvary and L. Markó, Organometallics, 1 (1982) 1120.

[16] J. Palágyi and L. Markó, J. Organomet. Chem., 236 (1982) 343.

[17] J.M. Brown and A.G. Kent, J. Chem. Soc., Perkin Trans. II, (1987) 1597.

[18] A.T. Jurewicz, L.D. Rollmann and D.D. Whitehurst, in D. Forster and J.F. Roth, (Eds.), Homogeneous Catalysis II, Advances in Chemical Series, Vol. 132, American Chemical Society, Washington, DC, 1974, p. 240.

[19] T. Okano, M. Makino, H. Konishi and J. Kiji, Chem. Lett., (1985) 1793.

[20] P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino, (Eds.) Organic Syntheses via Metal Carbonyls, Vol. 2, Interscience, New York, 1977, p. 183.

[21] B.T. Heaton, J.A. Iggo, C. Jacob, J. Nadarajah, M.A. Fontaine, R. Messere and A.F. Noels, J. Chem. Soc., Dalton Trans., (1994) 2875.

[22] J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987, p. 619.