CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201203069

Carbodeoxygenation of Biomass: The Carbonylation of Glycerol and Higher Polyols to Monocarboxylic Acids

Timur Coskun, Christopher M. Conifer, Laura C. Stevenson, and George J. P. Britovsek*[a]

Abstract: Glycerol is converted to a mixture of butyric and isobutyric acid by rhodium- or iridium-catalysed carbonylation using HI as the co-catalyst. The initial reaction of glycerol with HI results in several intermediates that lead to isopropyl iodide, which upon carbonylation forms butyric and isobutyric acid. At low HI concentration, the intermediate allyl iodide undergoes carbonylation to give vinyl acetic acid and crotonic acid. Higher polyols $C_nH_{n+2}(OH)_n$ are carbonylated to the corresponding C_{n+1} mono-carboxylic acids.

Keywords: butyric acid · carbon monoxide · carbonylation · glycerol · iridium · rhodium

Introduction

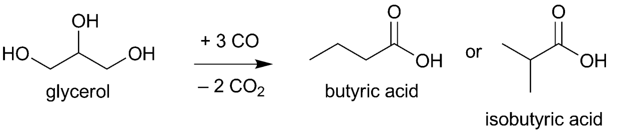
The development of new catalytic processes for the conversion of biomass into biofuels and biochemicals is currently of great interest.[1–3] Biodiesel is the second most produced biofuel after bioethanol and accounted for 27.5 % of the global biofuels output in 2011.[4] A major drawback of biodiesel is the production of approximately 1 kg of glycerol as a by-product for every 9 kg of biodiesel. As a consequence, research into new conversion processes for glycerol as a C_3 platform chemical into value-added products is therefore, both from an economical and environmental point of view, of considerable importance.[5] Besides gasification to syngas,[6] several conversions of glycerol are already being explored, for example, hydrogenolysis to 1,2- and 1,3-propanediol or the oxidation to dihydroxyacetone.[7–11] Other potential products that are being considered are acrylic acid, glycerol carbonate and epichlorohydrin.[5]

Biomass-derived compounds such as glycerol are oxygen rich and de-oxygenation is usually carried out by reaction with H_2 and the formation of H_2O, generally termed hydrodeoxygenation [Eq. (1)].[10] An alternative strategy, which is used here, is carbodeoxygenation: the carbonylation with CO and the formation of CO_2 [Eq. (2)]. The cost of CO and H_2 are comparable, but the product spectrum from carbodeoxygenations will be different and complementary to the products obtained through hydrodeoxygenation. Carbonylation reactions are widespread in the chemical industry, for example, in the production of acetic acid from methanol in the Monsanto and Cativa processes, and the underlying mechanisms for the carbonylation of lower alcohols are now well understood.[12–15] The carbonylation of higher alcohols, and in particular polyols, has received much less attention so far.[16–23] We therefore decided to investigate the application of carbonylation for the carbodeoxygenation of biomass-derived polyols, starting with glycerol.

$$\text{Hydrodeoxygenation: Biomass} + H_2 \rightarrow \begin{matrix}\text{Deoxygenated}\\ \text{Biomass}\end{matrix} + H_2O \qquad (1)$$

$$\text{Carbodeoxygenation: Biomass} + CO \rightarrow \begin{matrix}\text{Deoxygenated}\\ \text{Biomass}\end{matrix} + CO_2 \qquad (2)$$

The first studies on the carbonylation of glycerol were reported by Nakamura in 1979.[24] A rhodium complex $[\{RhCl(CO)_2\}_2]$ was used in combination with HI as the co-catalyst at 180 °C and 35 bar CO pressure and glycerol was converted after 80 min to a mixture of 45 mol % butyric (BA) and 30 mol % isobutyric acid (IBA), according to the overall reaction given in Equation (3). The only other report in the literature on the carbonylation of glycerol is a recent high-throughput study by Schunk and co-workers, who used $[\{RhCl(CO)_2\}_2]$ and CH_3I as the catalyst system and observed the formation of unsaturated acids such as vinyl acetic acid (VA) and crotonic acid (CA), in addition to the saturated acids BA and IBA.[22]



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[a] Dr. T. Coskun, Dr. C. M. Conifer, L. C. Stevenson, Dr. G. J. P. Britovsek
Department of Chemistry
Imperial College London, Exhibition Road
South Kensington, London SW7 2AZ (UK)
Fax. (+44) 20-75945804
E-mail: g.britovsek@imperial.ac.uk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203069.

The saturated and unsaturated C_4 acids are not the products one would immediately predict from the carbonylation of glycerol and no explanation has been provided so far for this surprising transformation. We present here the results of our extensive study on the carbonylation of glycerol, including mechanistic studies and a comparison between the performance of rhodium versus iridium-based catalysts. This systematic study demonstrates that both catalyst systems can give selective conversion of glycerol to a mixture of BA and IBA. While these C_4 acids are of industrial interest as esters in solvent applications, they could also be converted to other valuable chemicals such as butanol/isobutanol, butyraldehyde or methacrylic acid.

Results and Discussion

Carbonylation studies: Carbonylation experiments were carried out in acetic acid/water at various pressures (20–45 bar) and temperatures (130–180 °C), selected runs are listed in Table 1. In acetic acid, glycerol is rapidly acetylated to a mixture of mono-, di- and triacetoxyesters. For convenience, we therefore used the less viscous triester triacetin (1,2,3-triacetoxypropane, T) as the substrate, which gave very similar results as glycerol (for example, see runs 3 vs. 5). In our initial experiments, [{RhCl(CO)$_2$}$_2$] was used in combination with CH_3I as the co-catalyst. At 130 °C and 30 bar CO pressure, a mixture of eight products was obtained after 5 h, which were identified as the saturated acids (BA and IBA), the unsaturated acids (VA and CA), as well as allyl acetate (AA), allyl iodide (AI), isopropyl acetate (IPA) and isopropyl iodide (IPI), together with 38 mol % unreacted T (see run 1 and Figure 1).

Table 1. Results of the rhodium- and iridium-catalysed carbonylation reactions[a].

Run	Sub	Co	Cat	*T* [°C]	*t* [h]	All products [mol %] IBA	BA	IPA	IPI	AA	AI	PA	PI	CA	VA	T	Total [mol %]
1[b]	T	CH_3I	[Rh]	130	5	1.3	1.6	22	13	4.9	2.1	0	0	5.5	8.1	38	96
2[b]	T	HI	[Rh]	130	5	5.8	4.6	57	33	0	0	0	0	0	0	0	100
3[b]	T	HI	[Rh]	180	5	26	44	5.2	5.9	0	0	0.6	1.7	0	0	0	83
4[b]	T	HI	[Rh]	180	17	41	59	0	0	0	0	0	0	0	0	0	100
5[b]	G	HI	[Rh]	180	5	35	63	1.0	1.5	0	0	0	0	0	0	0	100
6[c]	T	CH_3I	[Ir]	130	5	0.1	0.1	0	0	30	4.8	0	0	0.3	0.3	14	49
7[c]	AA	CH_3I	[Ir]	180	5	14	12	1.0	5.5	0	0	0.5	0.5	0	0	0	33
8[c]	T	HI	[Ir]	130	5	0.4	0.5	12	6.1	14	18	0	0	0	0	0	51
9[c]	T	HI	[Ir]	150	5	6.5	8.0	31	11	0	0	0	0	0	0	0	56
10[c]	T	HI	[Ir]	180	5	13	15	2.9	2.0	0	0	0	0	0	0	0	33
11[c]	T	HI	[Ir]	180	17	17	18	0	0	0	0	0	0	0	0	0	35
12[c]	T	CH_3I	[Ir]	180	17	8.1	6.7	11	12	0	0	0.7	2.3	0	0	0	40
13[d]	T	HI	[Ir]	180	5	31	44	7.8	7.9	0	0	1.0	4.8	0	0	0	96
14[e]	T	HI	[Ir]	180	5	7.5	9.8	11	16	0	0	0.9	7.8	0	0	0	53
15[f]	T	HI	none	180	17	16	14	4.2	4.5	0	0	0	0	0	0	0	39

[a] Sub = Substrate (T = triacetin, G = glycerol, AA = allyl acetate); Co = Co-catalyst; Cat = Catalyst: [Rh] = [RhCl(CO)$_2$]$_2$ and [Ir] = [NBu$_4$][IrCl$_2$(CO)$_2$]. [b] Conditions: [RhCl(CO)$_2$]$_2$ (0.05 mmol), CH_3I (13 mmol) or HI (57 wt %, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL), CO (30 bar). [c] Conditions: [NBu$_4$][IrCl$_2$(CO)$_2$] (0.1 mmol), CH_3I (13 mmol) or HI (57 wt %, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL), CO (30 bar). [d] Promotor [Ru$_3$(CO)$_{12}$], (127 mg, 0.2 mmol) was added. [e] Instead of CO, syngas was used (CO/H_2, 3:1, 40 bar pressure). [f] no catalyst, HI (57 wt %, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL).

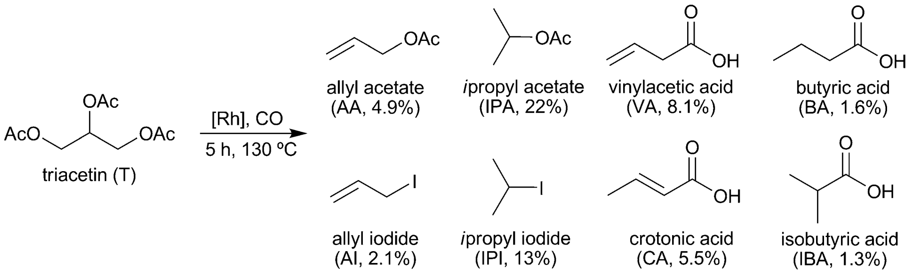


Figure 1. Product distribution from the carbonylation of triacetin (run 1 in Table 1, all values in mol %).

In the experiments with CH_3I as the co-catalyst, the HI required for the C–O bond activation is formed in situ by the carbonylation of CH_3I and hydrolysis. Schunk and coworkers, who also used CH_3I, noted that the carbonylation of glycerol was affected by the amount of water in the system: at low water concentration, significant amounts of the unsaturated C_4 acids VA and CA were obtained, whereas a higher water concentration led to the formation of BA and IBA.[22] In our experiments under the same conditions as in run 1, a significant improvement was observed when HI was used as the co-catalyst (run 2). Full conversion of triacetin was observed and no unsaturated acids were obtained. Increasing the temperature to 180 °C and prolonged reaction times resulted in the conversion to BA and IBA as the major reaction products (runs 3 and 4). It is tempting to propose that the unsaturated acids VA and CA could be intermediates in the formation of BA and IBA by isomerisation and hydrogenation (through the water–gas shift reaction). However, the presence of IPI and IPA, and *n*-propyl iodide (PI) and *n*-propyl acetate (PA) at higher temperatures (see run 3), are not easily explained by this mechanism.

The iridium-catalysed carbonylation reaction with [NBu$_4$][IrCl$_2$(CO)$_2$] in combination with CH_3I as the co-catalyst, at 130 °C and 30 bar CO pressure, produced mainly AA and AI, and small amounts of the acids (run 6). In a separate experiment (run 7), in which AA was used as the substrate, it was confirmed that AA is indeed an intermediate in the

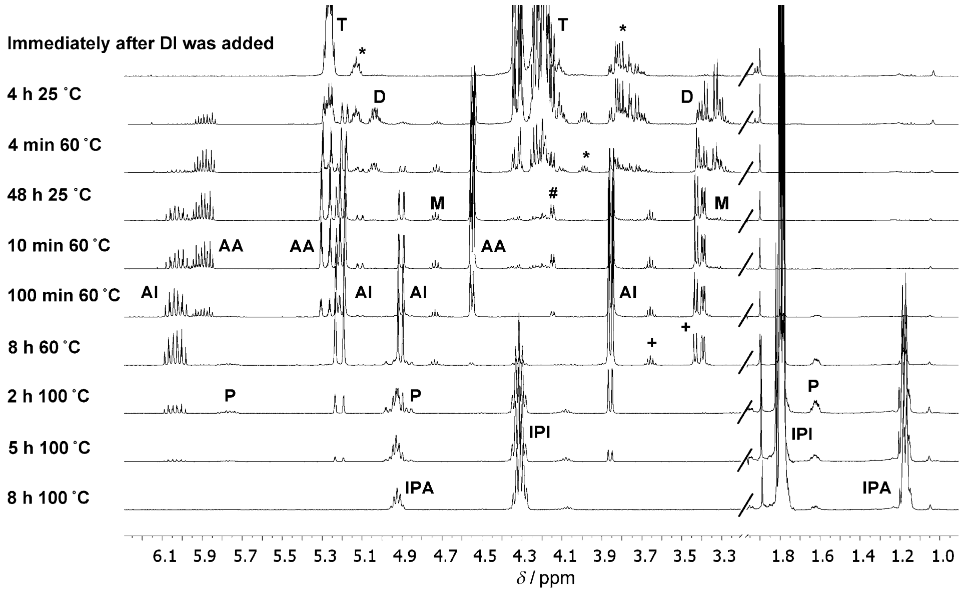


Figure 2. ^{1}H NMR spectra of the reaction of triacetin (T) with ten equivalents of DI (53 % in D_2O) in CD_3COOD (for labels, see Figure 3; * = triacetin hydrolysis products, # = allyl alcohol, + = 1,3-diiodo-2-propanol).

formation of BA and IBA. Using HI as the co-catalyst resulted in an increased yield of BA and IBA, which was further improved by raising the temperature (runs 8–10) and longer reaction times (run 11). Under these conditions, HI is clearly a superior co-catalyst than CH_3I (runs 8 vs. 6 and 11 vs. 12).

It should be noted that under the same conditions as run 11, but in the absence of a metal catalyst, carbonylation took place due to HI by the Koch reaction (run 15).[25] The results from run 11 are only marginally better than this blank experiment without a metal catalyst. It is well known that iridium-based carbonylation catalysts rapidly deactivate due to the formation of $[IrI_4(CO)_2]^-$ and promotors are needed that can reversibly bind iodide in order to regenerate the deactivated catalyst.[26] Indeed, orange crystals obtained at the end of several runs were identified as $[NBu_4][IrI_4(CO)_2]$ by IR spectroscopy (ν(CO) = 2109 and 2071 cm^{-1}).[15] The best results for iridium were obtained in the presence of the promotor $[Ru_3(CO)_{12}]$ (run 13). These results are comparable to those obtained with the rhodium-based catalyst under the same conditions (run 13 vs. 3). Instead of CO, syngas (CO/H_2 = 3:1) was used in run 14 for the carbonylation reaction, but gave inferior results. Experiments at different pressures have shown that the BA/IBA ratio increases with increasing pressure, similar to the observations reported by Dekleva and Forster for the carbonylation of *n*-propanol and isopropanol.[16,17]

Mechanistic studies: Despite the presence of three hydroxyl functionalities in glycerol, carbonylation results exclusively in monocarboxylic acids, rather than tricarboxylic acids. Similarly, the carbonylation of 1,2-diols, such as glycol, 1,2-propane diol and cyclohexane diol, produce only monocarboxylic acids.[22,23] In order to explain this surprising selectivity, we have investigated the reaction of triacetin with HI in acetic acid by ^{1}H NMR spectroscopy. First investigations on the reaction of glycerol with HI date back to the 19th century,[27,28] and a study in the 1950s revealed that allyl iodide is an intermediate in the reaction and that eventually isopropyl iodide is formed.[29] We have revisited this reaction under conditions that are similar to those used for the carbonylation experiments. The product mixture that is formed upon reacting triacetin with ten equivalents of DI (53 % in D_2O) in CD_3COOD was monitored by ^{1}H NMR spectroscopy (see Figure 2). Over time and with increasing temperature, besides partial hydrolysis to di- and monoacetylated glycerol that were easily identified,[30] the sequence of transformations shown in Figure 3 is observed. Double nucleophilic substitution results in the formation of 1,3-diiodo-2-acetyl propane (M), which is followed by elimination of iodine and a 2,1-shift of the acyl group to the terminal position to give allyl acetate (AA).[31] Similar observations and formation of allyl acetate have been reported from the reaction of 1,3-dichloro-2-acetyl propane with sodium iodide.[32] Further substitution results in allyl iodide (AI) and addition of DI followed by elimination of I_2 generates propene (P), which undergoes addition of DI to give finally isopropyl iodide (IPI), together with some isopropyl acetate (IPA). Oxidative addition of IPI at rhodium and iridium results in isomerisation to both isopropyl and *n*-propyl metal complexes,[33] and as a result, the carbonylation of IPI results in the formation of both BA and IBA. It should be noted that at higher temperatures (180 °C) small amounts of *n*-propyl iodide are observed in the reaction mixture, which suggests that CO insertion competes with reductive elimination at these temperatures.

Several observations support the proposed reaction sequence in Figure 3. Whilst the conversion of triacetin in runs 8–12 was quantitative, the total amount of product recovered from the liquid phase at the end of the reaction did not exceed 56 mol %. Qualitative analysis of the gas phase by GC and ^{1}H NMR analysis at the end of these runs revealed the presence of propene, which would explain the observed carbon imbalance in these experiments. Noteworthy, propene was also observed by Dekleva and Forster in the carbonylation of *n*-propanol and isopropanol.[16,17] It can be seen from Figure 2 that the reaction of DI with allyl iodide (AI) and with propene (P) to give IPI are slow and require extensive heating at 100 °C. These reactions will be acceler-

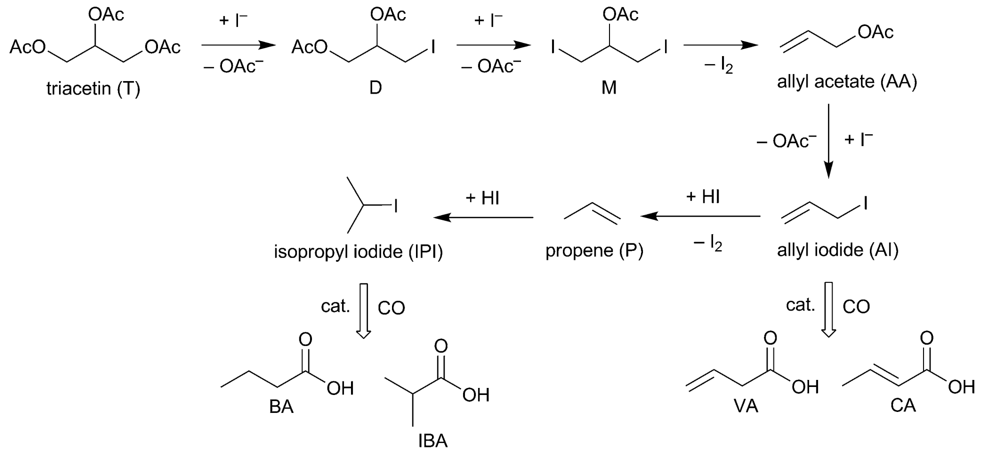
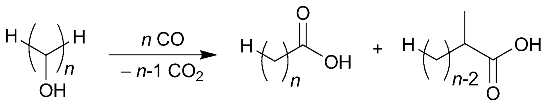


Figure 3. Sequence of intermediates and products from the reaction of triacetin with HI.

ated at higher HI concentrations and increased temperature. The formation of the unsaturated acids VA and CA are the products observed at low temperature, short reaction times and CH_3I as the co-catalyst and must therefore originate from the carbonylation of AI, before further conversion of AI to IPI can take place (see Figure 3). Conversely, the use of HI as the co-catalyst, higher temperatures and longer reaction times favour the formation of IPI and result in the carbonylation to the saturated acids BA and IBA exclusively.

The overall reaction of glycerol to IPI requires five equivalents of iodide and generates two equivalents of iodine (see Figure 3). Iodide was added to the reactor either in the form of HI or CH_3I, but only 0.5 equivalents of iodide was used in all runs relative to triacetin, which implies that I_2 must be reduced in situ back to I^-. The reductant is believed to be either H_2, formed by the water–gas shift reaction,[34] and the reaction of I_2 with H_2 to HI is catalysed by rhodium or iridium complexes.[35,36] It is also possible that I_2 reacts with $[IrI_2(CO)_2]^-$ to give $[IrI_4(CO)_2]^-$, which can react with CO and water to regenerate the catalyst $[IrI_2(CO)_2]^-$ together with CO_2 and two molecules of HI.[34] The use of syngas (CO/H_2) instead of CO (run 14) was also investigated, but did not lead to better conversion. Deactivation of the iridium catalyst is likely to prevent both carbonylation and iodide re-activation.[37] Noteworthy, the reduction of glycerol with HI to allyl iodide and I_2 is related to the recently revisited di-dehydroxylation reaction of glycerol to allyl alcohol with formic acid, whereby formic acid acts as the stoichiometric reductant.[38]

The sequence of reactions shown here for triacetin in Figure 3 also applies to other 1,2-diols and higher polyols resulting in the formation of mono-iodo alkanes. ^{1}H NMR analysis of the reaction of ethylene glycol with six equivalents of DI in CD_3COOD has shown the formation of ethylene as an intermediate and ethyl iodide as the final product (see Figure S1 in the Supporting Information). Preliminary results on the carbonylation of erythritol $C_4H_6(OH)_4$ under the same conditions as for run 3 in Table 1, resulted in the formation of pentanoic acid (3.3 mol %) and 2-methylbutyric acid (5.2 mol %). The lower conversion in this case is believed to be due to the lower effective iodide concentration, as seven equivalents of iodide are needed in this case to reduce erythritol to 2-iodobutane. Furthermore, the reaction of sorbitol $C_6H_8(OH)_6$ with HI has been reported to generate 2-iodo hexane.[39] Nakamura reported that the carbonylation of ethylene glycol resulted in propionic acid and that sorbitol gave the isomeric C_7 acids heptanoic acid and 2-methyl hexanoic acid.[24] Taking all these results into account, the following general reaction can be postulated for the carbodeoxygenation of polyols as shown in Equation (4). For methanol ($n=1$) only one product, acetic acid, is obtained, which is the industrially applied Monsanto or Cativa process. Also for ethylene glycol ($n=2$) only one product, propionic acid, is formed, whereas for higher polyols for which $n>2$, a mixture of two isomeric C_{n+1} monocarboxylic acids is obtained.



(4)

Conclusion

The catalyst systems $[\{RhCl(CO)_2\}_2]$ in combination with the co-catalyst HI, or $[IrCl_2(CO)_2]^-$ together with the promotor $[Ru_3(CO)_{12}]$ and HI, can carbonylate glycerol to butyric and iso-butyric acid with comparable activities and selectivities. A key intermediate, allyl acetate, is formed prior to the actual carbonylation reaction by the reduction of glycerol with HI. At low HI concentration, allyl acetate is carbonylated to vinyl acetic acid and crotonic acid, whereas at higher HI concentrations allyl acetate is converted to isopropyl iodide, which is carbonylated to butyric and isobutyric acid. The carbonylation reaction can be applied to higher polyols $C_nH_{n+2}(OH)_n$ to give the corresponding C_{n+1} monocarboxylic acids. We are currently investigating conversions of other biomass-derived platform chemicals to value-added products using this carbodeoxygenation strategy.

Experimental Section

General procedures and characterisation data for selected compounds can be found in the Supporting Information.

Acknowledgements

We thank the Department of Chemistry at Imperial College London for financial support and Johnson Matthey for a generous loan of rhodium and iridium salts. We thank Dr. Ayako Miyazaki for the translation of reference [24] and Dr. Glenn Sunley for helpful discussions.

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Received: August 29, 2012
Revised: February 19, 2013