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Carbo-deoxygenation of Biomass: The Carbonylation of Glycerol and Higher Poly-ols to Mono-carboxylic Acids

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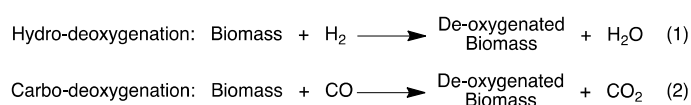
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Abstract

Glycerol is converted to a mixture of butyric and iso-butyric acid via the 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 poly-ols $C_nH_{n+2}(OH)_n$ are carbonylated to the corresponding C_{n+1} mono-carboxylic acids.

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 accounts for 27.5% of the global biofuels output in 2011.[4] A major drawback of biodiesel is the production of ca. 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 from an 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 epichlorhydrin.[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 hydro-deoxygenation (Eq. 1).[10] An alternative strategy, which is used here, is carbo-deoxygenation: 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 carbo-deoxygenations will be different and complementary to the products obtained via hydro-deoxygenation. Carbonylation reactions are widespread in the chemical industry, for example in the production of acetic acid from methanol in the Monsanto and Cativa process, 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 carbo-deoxygenation of biomass-derived polyols, starting with glycerol.

$$\text{Hydro-deoxygenation: Biomass} + H_2 \longrightarrow \text{De-oxygenated Biomass} + H_2O \quad (1)$$

$$\text{Carbo-deoxygenation: Biomass} + CO \longrightarrow \text{De-oxygenated Biomass} + CO_2 \quad (2)$$

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 minutes to a mixture of 45 mol% butyric (BA) and 30 mol% isobutyric acid (IBA), according to the overall reaction given in

Eq. 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 MeI 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] 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 will show 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.
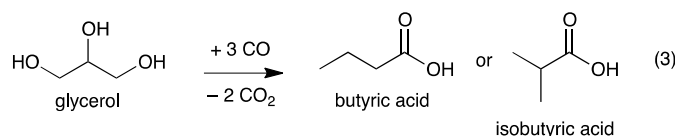
Results and Discussion

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 the acetic acid solvent, glycerol is rapidly acetylated to a mixture of mono-, di- and triacetoxy-esters. For convenience, we therefore used the less viscous tri-ester triacetin (1,2,3-triacetoxypropane, T) as the substrate, which gave essentially the same results as glycerol (see for example runs 3 vs. 5). In our initial experiments, $[RhCl(CO)_2]_2$ was used in combination with MeI as the co-catalyst. At 130 °C and 30 bar CO pressure, a mixture of eight products was obtained after 5 hours, 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).

In the case of MeI as the co-catalyst, HI required for the C-O bond activation is formed *in situ* via the carbonylation of MeI and hydrolysis. Schunk and co-workers, who also used

MeI, 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 (via the WGSR). 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.
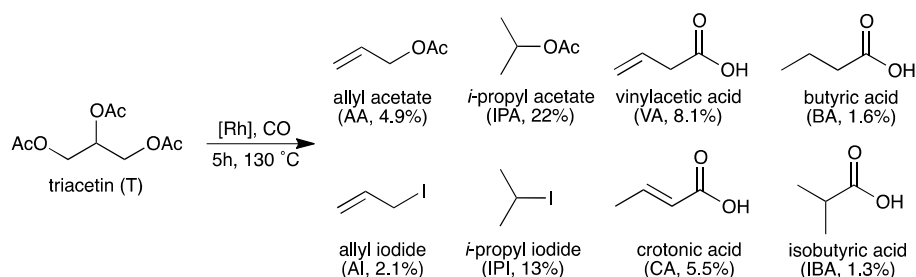

Figure 1. Product distribution from the carbonylation of triacetin (run 1 in Table 1, all values in mol%).

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

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

Sub. = Substrate; Co. = Co-catalyst; Cat. = Catalyst: [Rh] = [RhCl(CO)$_2$]$_2$ and [Ir] = [NBu$_4$][IrCl$_2$(CO)$_2$]. a) Conditions: [RhCl(CO)$_2$]$_2$ (0.05 mmol), MeI (13 mmol) or HI (57 wt%, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL), CO (30 bar). b) Conditions: [NBu$_4$][IrCl$_2$(CO)$_2$] (0.1 mmol), MeI (13 mmol) or HI (57

wt%, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL), CO (30 bar). c) Promotor [Ru$_3$(CO)$_{12}$], (127 mg, 0.2 mmol) was added. d) Instead of CO, syngas was used (CO/H$_2$, 3/1, 40 bar pressure). e) no catalyst, HI (57 wt%, 13 mmol), triacetin (27 mmol), acetic acid (6.7 mL), water (1.5 mL).

The iridium-catalysed carbonylation reaction with [NBu$_4$][IrCl$_2$(CO)$_2$] in combination with MeI 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), where AA was used as the substrate, it was confirmed that AA is indeed an intermediate in the 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 MeI (cf. runs 5 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 *via* 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 (ν(CO) = 2109 cm^{-1} 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 (cf. 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 *i*-propanol.[16,17]

Mechanistic Studies

Despite the presence of three OH functionalities in glycerol, carbonylation results exclusively in mono-carboxylic acids, rather than tri-carboxylic acids. Similarly, the carbonylation of 1,2-diols such as glycol, 1,2-propane diol and cyclohexane diol produce only mono-carboxylic 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 10 equiv. 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-acetylated and mono-acetylated glycerol which 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 at these temperatures, CO insertion competes with reductive elimination.
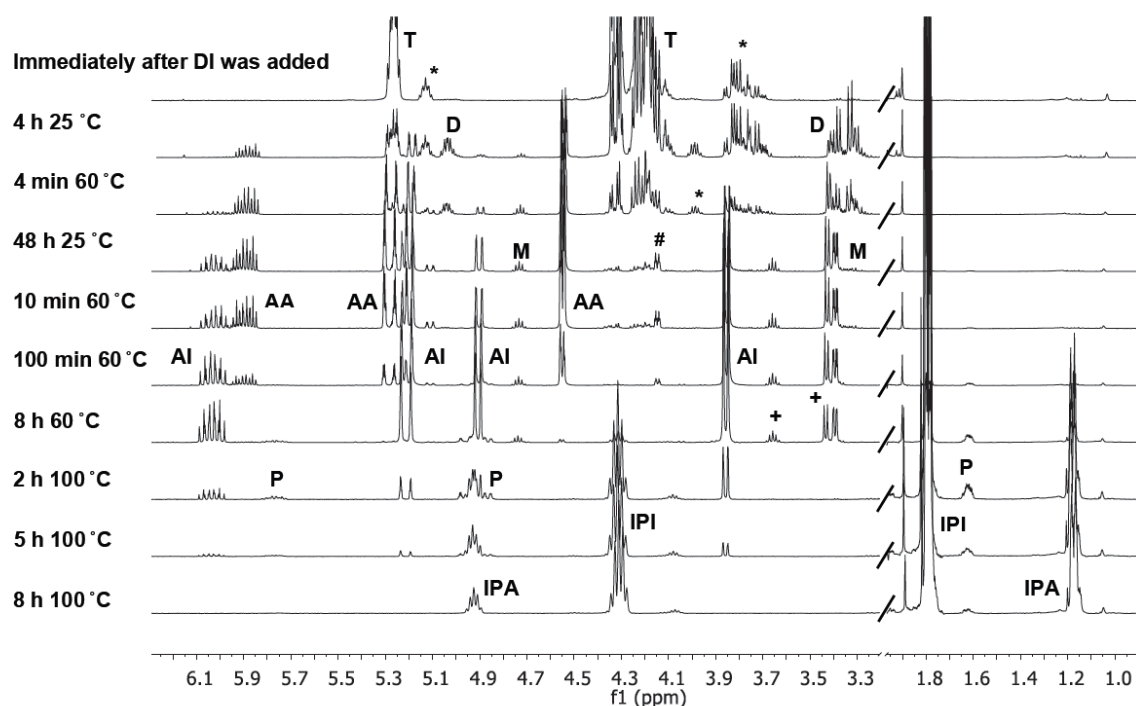
Figure 2. ^{1}H NMR spectra of the reaction of triacetin T with 10 equiv. DI (53% in D$_2$O) in CD$_3$COOD (for labels, see Figure 3; * = triacetin hydrolysis products, # = allyl alcohol, + = 1,3-diiodo-2-propanol).

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 i-propanol.[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 accelerated 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 MeI 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 5 equiv. iodide and generates 2 equiv. iodine (see Figure 3). Iodide was added to the reactor either in the form of HI or MeI but only 0.5 equiv. 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 via the WGSR,[34] and the reaction of I_2 with H_2 to HI is catalysed by rhodium or iridium complexes.[35,36] Alternatively, certainly for Ir it is 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 2 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]
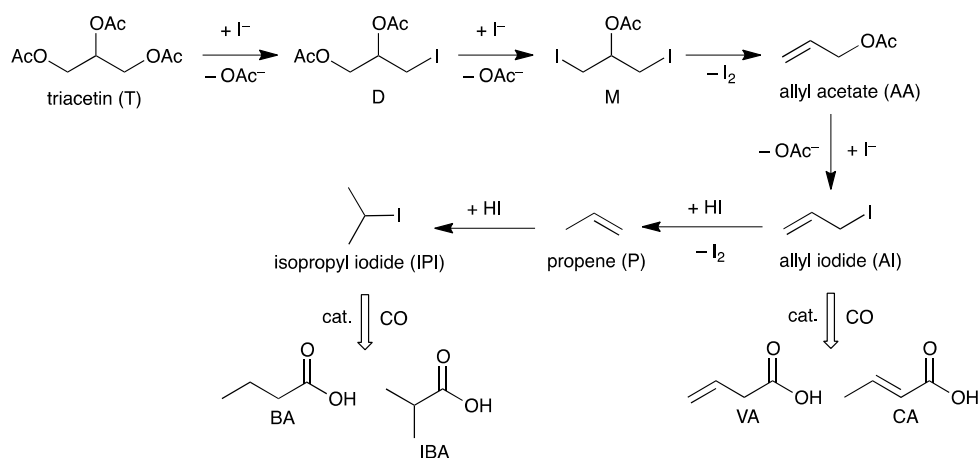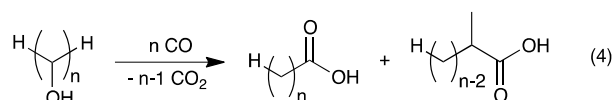

Figure 3. Sequence of intermediates and products from the reaction of triacetin with HI.

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 6 equiv. DI in CD_3COOD has shown the formation of ethylene as an intermediate and ethyl iodide as the final product (See Figure S1). Preliminary results on the carbonylation of erythritol $C_4H_6(OH)_4$ have shown the formation of pentanoic acid and 2-methylbutyric acid. Furthermore, the reaction of sorbitol $C_6H_8(OH)_6$ with HI has

been reported to generate 2-iodo hexane.[39] Nakamura reported the carbonylation of ethylene glycol to give propionic acid and of sorbitol to give heptanoic acid and 2-methyl hexanoic acid.[24] Taking all these results into account, the following general reaction can be postulated for the carbo-deoxygenation of poly-ols as shown in eq. 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 poly-ols where n>2, a mixture of two isomeric C_{n+1} mono-carboxylic acids is obtained.

$$H \left(\right)_n \!\!\!\! {}^{H}_{OH} \xrightarrow[-\,n{-}1\ CO_2]{n\ CO} H \left(\right)_n \!\!\!\! \overset{O}{\underset{OH}{\parallel}} + H \left(\right)_{n{-}2} \!\!\!\! \overset{}{\underset{O}{}} OH \quad (4)$$

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 *via* 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 poly-ols $C_nH_{n+2}(OH)_n$ to give the corresponding C_{n+1} mono-carboxylic acids. We are currently investigating conversions of other biomass-derived platform chemicals to value-added products using this carbo-deoxygenation strategy.

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TOC Entry

glycerol $\xrightarrow[- 2\ CO_2]{+\ 3\ CO}$ butyric acid or isobutyric acid
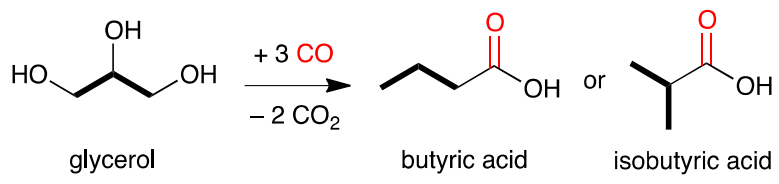
Supporting Information

Carbo-deoxygenation of Biomass: Carbonylation of Glycerol and Higher Poly-ols to Mono-carboxylic Acids

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General

All moisture and oxygen sensitive compounds were prepared using standard high vacuum line, Schlenk and cannula techniques. A standard nitrogen-filled glove box was used for any subsequent manipulation and storage of these compounds. Standard ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV400 spectrometer. ^{1}H NMR chemical shifts were referenced to the residual non-deuterated solvent signal and ^{13}C NMR chemical shifts to the signal of the deuterated solvent. FTIR spectra were measured using a Perkin Elmer Spectrum GX spectrometer. Elemental analyses were performed by the Science Technical Support Unit at The London Metropolitan University. Quantitative GC analysis was performed using an Agilent 6890A gas chromatograph and an Innowax (30 m x 0.25 mm, film thickness 0.25 mm) column. Acetonitrile was used as the standard for quantitative analysis and product identities were confirmed by comparison with authentic samples and by GC-MS.

Solvents and Reagents

Diethyl ether and tetrahydrofuran were dried by prolonged reflux, under a nitrogen atmosphere, over sodium metal with a benzophenone ketyl indicator and distilled freshly prior to use. Dichloromethane, acetonitrile, hexane and methyl iodide were dried over calcium hydride and distilled under nitrogen. [Rh(CO)$_2$Cl]$_2$ and [NBu$_4$][Ir(CO)$_2$Cl$_2$] were prepared according to published procedures.[1] All other chemicals, including triacetin, glycerol and methyl iodide were used as received.

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Carbonylation reactions

General Procedure for the Carbonylation reaction

A 100 mL glass reactor sleeve charged with catalyst, solvent, water, iodide co-catalyst, starting material as given in Table 1 and stirrer bar was placed into a 100 mL high pressure Hastelloy steel Parr autoclave. The reactor was sealed and purged with CO or CO/H_2 three times. The reactor was then pressurized to the desired pressure and closed. The temperature was set by a thermocouple, which measure the temperature inside the reactor and the reactor was heated to the required temperature. Recorded reaction times refer to the time that the reaction was at the desired temperature, not including the time required to reach this temperature. After the desired reaction time the reactor was allowed to cool with the assistance of a water bath. Once at room temperature the reactor was vented slowly into a fume cupboard.

GC Analysis

Quantitative analysis of the product mixture was carried out by gas chromatography. Relative response factors were calculated for each product from genuine samples using acetonitrile as a reference.

Example carbonylation reaction

Triacetin (5.9 g, 27 mmol), $[Bu_4N][Ir(CO)_2Cl_2]$ (56 mg, 0.1 mmol), acetic acid (6.5 g), methyl iodide (1.88 g, 13.2 mmol) and water (1.5 g) were added to the reactor. The reactor was sealed, purged with CO, pressurized with 30 bar of CO and heated to 130 °C. After 17 hours the reactor was allowed to cool down to room temperature showing a pressure of 15 bar. The reactor was vented in a well ventilated fume cupboard and the product mixture was analysed by the GC and GC/MS.

NMR experiments

General procedure for reactions carried out in Young's tap NMR tube with deuterium iodide

The starting material was weighed into a vial, the required amount of deuterated acetic acid solvent added and the solution transferred to a Young's tap NMR tube. An NMR spectrum was taken before any iodide was added. Deuterium iodide solution 53 wt. % in D_2O was then weighed and added to the NMR tube. When the NMR tube needed to be heated this was done in an oil bath up to temperatures of 120 °C. The reactions were followed by ^{1}H NMR spectroscopy.

Triacetin:

Isopropyl acetate (IPA): ^{1}H NMR (400 MHz, CD_3COOD) δ 4.96 (sep, *J* = 8.0, 1H, C*H*), 1.98 (s, 3H, COOC*H*$_3$), 1.18 (d, *J* = 8.0, 6H, CHC*H*$_3$).

Allyl Iodide (AI): ^{1}H NMR (400 MHz, CD_3COOD) δ 6.07 (m, 1H, CH_2CHCH_2), 5.24 (dd, *J* = 16.0, 1.2, 1H, CH*H*CHCH$_2$), 5.94 (dd, *J* = 15.2, 1.2, 1H, C*H*HCHCH$_2$), 3.88 (dd, 2H, C*H*$_2$I).

Propene (P): ^{1}H NMR (400 MHz, CD_3COOD) δ 5.80 (m, 1H, CH_2CHCH_3), 5.01 (ddq, $J = 16.0$, 1H, $CHHCHCH_3$). 4.92 (ddq, $J = 16.0$, 1H, $CHHCHCH_3$), 1.69 (app dt, $J = 6.4$, 1.6, 3H, CH_2CHCH_3).

Isopropyl Iodide (IPI): ^{1}H NMR (400 MHz, CD_3COOD) δ 4.37 (sep, $J = 8.0$, 1H, CH), 1.88 (d, $J = 8.0$, 6H, CH_3CHCH_3).

Allyl Acetate (AA): ^{1}H NMR (400 MHz, CD_3COOD) δ 5.93 (m, 1H, CH_2CHCH_2), 5.31 (dd, $J = 17.0$, 2.0, 1H, $CHHCHCH_2$), 5.21 (dd, $J = 10.4$, 1.6, 1H, $CHHCHCH_2$), 4.57 (app dt, $J = 5.6$, 1.6, 2H, CH_2COOCH_3), 2.07 (s, 3H, $COOCH_3$).

1, 2, 3-propanetriol, 1,2-diacetate: ^{1}H NMR (400 MHz, CD_3COOD) δ 5.12 (m, 1H, CH), 4.18 (m, 2H, CH_2OAc), 3.76 (m, 2H, CH_2OH), 2.08 (s, 3H, CH_2OCOCH_3), 2.06 (s, 3H, $CHCOCH_3$).

1, 2, 3-propanetriol, 1,3-diacetate: ^{1}H NMR (400 MHz, CD_3COOD) δ 4.08 (m, 4H, CH_2), 3.97 (m, 1H, CH).

1, 2, 3-propanetriol, 2-acetate: ^{1}H NMR (400 MHz, CD_3COOD) δ 4.95 (m, 1H, CH), 3.66 (m, 4H, CH_2).

Triacetin (T): ^{1}H NMR (400 MHz, CD_3COOD) δ 5.30 (m, 1H, CH), 4.34 (dd, $J = 12.0$, 4.0, 2H, $CHHCHCHH$), 4.23 (dd, $J = 12.2$, 6, 2H, $CHHCHCHH$), 2.10 (s, 3H, $CHCOOCH_3$), 2.09 (s, 6H, CH_2COOCH_3).

Glycerol (G): [1]H (400 MHz, CD_3COOD) δ 3.91 (1 H, s, CH), 3.76 (dd, $J = 4.1$, 11.8, 2H, $CHHCHCHH$), 3.71 (dd, $J = 6.3$, 11.8, 2H, $CHHCHCHH$).

Crotonic acid (CA): ^{1}H NMR (400 MHz, CD_3COOD) δ 7.11 (dq, $J = 15.5$, 6.8, 1H, CH_3CH), 5.87 (dq, $J = 15.5$, 1.6, 1H, $HCCOOH$), 1.89 (dd, $J = 6.8$, 1.6, 3H, H_3C).

Vinyl acetic acid (VA): ^{1}H NMR (400 MHz, CD_3COOD) δ 5.97 (m, 1H, CH_2CH), 5.16-5.23 (m, CH_2CHCH_2COOH), 3.17 (dt, $J = 6.8$, 1.6, 2H, CH_2COOH).

Butyric acid (BA): ^{1}H NMR (400 MHz, CD_3COOD) δ 2.36 (t, $J = 7.2$, 2H, CH_2COOH), 1.67 (app sex, $J = 3.8$, 2H, CH_2CH_2COOH), 0.98 (t, $J = 7.6$, 3H, CH_3).

2-acetoxy-1,3-diiodopropane (M): ^{1}H NMR (400 MHz, CD_3COOD) δ 4.73 (app quin, 1H, $J = 5.6Hz, CH$), 3.39 (dd, 4H, $J = 5.4$, 1.7 Hz, ICH_2).

2-hydroxy-1,3,-diiodopropane: ^{1}H NMR (400 MHz, CD_3COOD) δ 3.66 (quin, 1H $J = 5.4$ Hz, CH), 3.43 (d, 4H, $J = 5.5$ Hz, ICH_2).

Allyl alcohol: ^{1}H NMR (400 MHz, CD_3COOD) δ 4.15 (app dt, 2H, $J = 5.4$, 1.5 Hz, CH_2).

Ethylene glycol:

An NMR reaction was carried out utilising ethylene glycol (**19**) as the starting material and deuterium iodide as the iodide source. 3 equivalents of DI would be required to convert ethylene glycol (**19**) to iodoethane (**26**). In accordance with the conditions employed for the reactions with triacetin, twice the amount of DI needed was employed (6 equiv.). The solution was left at room temperature for 36 hours before gradually heating, starting at 60 °C and increasing up to 120 °C. Both the mono- and di- acetylated species ((**20**) and (**21**)) formed very quickly at room temperature. Substitution of the acetate groups with iodide then occurs to produce species (**22**) as the major product after 25 hours at room temperature. 1-Hydroxy-2-iodoethane (**23**) can also be identified but in smaller amounts, this could be formed by the direct substitution of ethylene glycol (**19**), however this is unlikely as the ethylene glycol appears to become acetylated relatively easily. Therefore, it is more likely to be species (**22**) that is hydrolysed as it is this species that builds up at room temperature.

Ethene was observed after heating at 80 °C for 20 minutes and once the temperature had been raised to 90 °C, 1,2-diiodoethane (**24**) was observed.
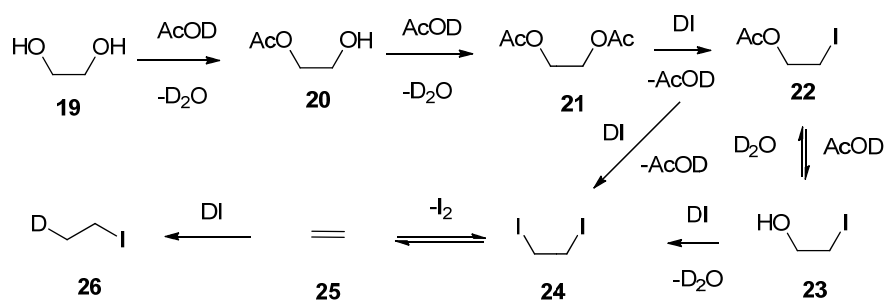
Scheme S1

On the reaction pathway shown in the above Scheme S1, diiodoethane (**24**) is formed first followed by elimination of iodine to yield ethene (**25**), despite this ethene is observed before diiodoethane. This suggests that the elimination of iodine to ethene occurs easily and thus diiodoethane (**24**) is only observed at higher temperatures, when the earlier substitution reactions occur faster, producing diiodoethane more rapidly. Iodoethane is observed after heating at 120 °C for 1 hour however the reaction does not go to 100% conversion, even after heating for 52 hours, ethene is observed. This indicates that, as was found for triacetin, the addition of DI across the double bond is slower than the other steps. The integration values of iodoethane again support the proposed mechanism, and the two signals integrate 1:1 indicating the presence of a deuterium atom on the methyl group. Furthermore, a complex splitting pattern is observed for the methyl protons, indicated the presence of a deuterium atom. Thus, it follows that when considering the carbonylation of ethylene glycol it is actually the carbonylation of iodoethane to propionic acid.
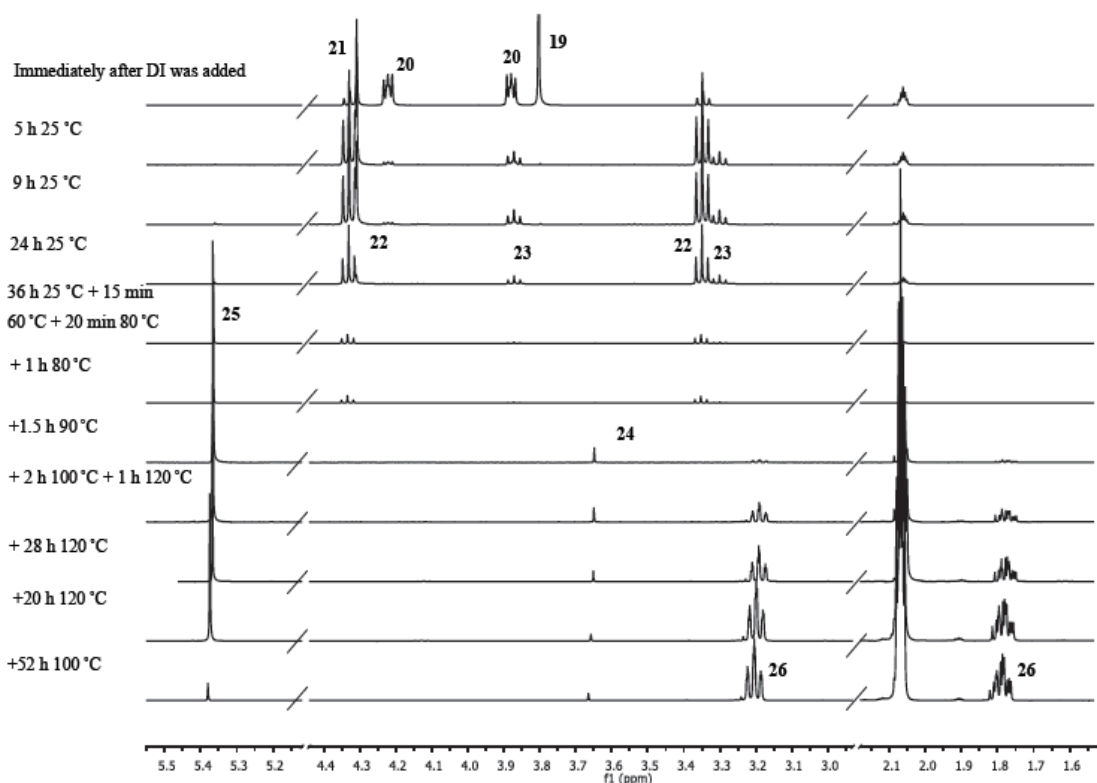
Figure S1. ^{1}H NMR spectra of the reaction of ethylene glycol with 6 equiv. DI (53% in D_2O) in CD_3COOD (for labels, see below).

Ethylene glycol (19):^{1}H NMR (400 MHz, CD_3COOD) δ 3.76 (s, 4H, CH_2).
Ethylene glycol diacetate (21):^{1}H NMR (400 MHz, CD_3COOD) δ 4.29 (s, 4H, CH_2).
Ethylene glycol monoacetate (20):^{1}H NMR (400 MHz, CD_3COOD) δ 4.20 (t, 2H, J = 4.6, CH_2OAc), 3.86 (t, 2H, J = 4.6, CH_2OH).
1, 2-diiodoethane (24):^{1}H NMR (400 MHz, CD_3COOD) δ 3.65 (s, 4H, CH_2).
Ethene (25):^{1}H NMR (400 MHz, CD_3COOD) δ 5.37 (s, CH_2).
Iodoethane (26):^{1}H NMR (400 MHz, CD_3COOD) δ 3.19 (q, 2H, J = 7.5, CH_2) 1.80 (t, 3H, J = 7.5, CH_3).
1-acetoxy-2-iodoethane (22):^{1}H NMR (400 MHz, CD_3COOD) δ 4.34 (t, 2H, J = 6.8, CH_2OAc), 3.32 (t, 2H, J = 6.8, CH_2I).
1-hydroxy-2-iodoethane (23): ^{1}H NMR (400 MHz, CD_3COOD) δ 3.87 (t, 2H, J = 6.8 Hz, CH_2I), 3.30 (t, 2H, J = 6.8 Hz, CH_2I).

Examples of GC Traces for Selected Runs
Run 1 in Table 1 (* solvent impurities in THF, which was used as diluent for GC analysis; MeCN was used as standard):

Run 13 in Table 1