Supporting Information

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

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**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. All other chemicals, including triacetin, glycerol and methyl iodide were used as received.

**References:**
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/H₂ 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), [Bu₄N][Ir(CO)₂Cl₂] (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 D₂O 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 ¹H NMR spectroscopy.

Triacetin:
Isopropyl acetate (IPA): ¹H NMR (400 MHz, CD₃COOD) δ 4.96 (sep, J = 8.0, 1H, CH), 1.98 (s, 3H, COOC₃H₇), 1.18 (d, J = 8.0, 6H, CHC₃H₇).
Allyl Iodide (AI): ¹H NMR (400 MHz, CD₃COOD) δ 6.07 (m, 1H, CH₂CH₂CH₂), 5.24 (dd, J = 16.0, 1.2, 1H, CHHCH₂CH₂), 5.94 (dd, J = 15.2, 1.2, 1H, CHHCH₂CH₂), 3.88 (dd, 2H, CH₂I).
Ethylene glycol:

An NMR reaction was carried out utilising ethylene glycol (19) as the starting material and deuterium oxide 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.

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$_2$O) in CD$_3$COOD (for labels, see below).

**Ethylene glycol (19):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 3.76 (s, 4H, CH$_2$).

**Ethylene glycol diacetate (21):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 4.29 (s, 4H, CH$_2$).

**Ethylene glycol monoacetate (20):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 4.20 (t, 2H, $J = 4.6$, CH$_2$OAc), 3.86 (t, 2H, $J = 4.6$, CH$_2$OH).

**1, 2-diiodoethane (24):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 3.65 (s, 4H, CH$_2$).

**Ethene (25):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 5.37 (s, CH$_2$).

**Iodoethane (26):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 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$_3$COOD) $\delta$ 4.34 (t, 2H, $J = 6.8$, CH$_2$OAc), 3.32 (t, 2H, $J = 6.8$, CH$_3$I).

**1-hydroxy-2-iodoethane (23):** $^1$H NMR (400 MHz, CD$_3$COOD) $\delta$ 3.87 (t, 2H, $J = 6.8$ Hz, CH$_2$I), 3.30 (t, 2H, $J = 6.8$ Hz, CH$_3$I).
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

- THF
- MeCN
- IPA
- IPI
- PA
- PI

Acetic acid  IBA  BA