Supporting Information

Experimental section

General. Tetrabutylphosphonium bromide was neutralized and dried before use, following our reported procedure.¹ In the reaction of 3-hydroxypropionic acid, a mixture of 3-hydroxypropionic acid in water and tetrabutylphosphonium bromide was dried before reaction, using the same drying procedure. All other chemicals were used as received: tetrabutylphosphonium bromide (Sigma-Aldrich, 98%), tetrabutylphosphonium hydroxide (TCI, 40% in water), n-hexane (Sigma-Aldrich, 97%), n-tetradecane (TCI, 99%), mesitylene (Acros Organics, 98%), N₂ (Air Liquide, α 1), HBr (Sigma-Aldrich, 48% in water), *N,O*-bis(trimethylsilyl)trifluoroacetamide (Sigma-Aldrich, BSTFA + TCMS 99:1), DL-lactic acid (Sigma-Aldrich, 90%), DL-lactide (Thermo Fischer, 99%), calcium lactate pentahydrate (J&K Scientific, 98%), methyl DL-lactate (Sigma-Aldrich, 97%), acrylic acid (Acros Organics, 99.5%, stabilized), 2-bromopropionic acid (Sigma-Aldrich, 99%), 3-bromopropionic acid (Sigma-Aldrich, 97%), 3-hydroxypropionic acid (TCI, 30% in water), H₂SO₄ (Merck, 98%), HBr (Acros Organics, 33% in acetic acid), aluminium acetylacetonate (Sigma-Aldrich, 99%), N-methylpyrrolidone (Acros, 99.5%, Extra Dry), Nafion NR50 (Sigma-Aldrich, ≥0.8 meq/g).

Gas chromatographic (GC) analysis. Substrate conversions and product yields were determined using GC analysis on a Shimadzu GC-2010 instrument with a 60 m CP SIL 5 CB column and an FID detector. The peak areas of substrate and products were normalized by dividing them by the peak area of an internal standard. For volatile compounds (boiling point <100 °C was chosen as the limit), n-hexane was used as internal standard to account for losses due to evaporation. Less volatile compounds were quantified using n-tetradecane. The yield of polar compounds was determined from the silylated samples. For the quantification of lactic acid and acrylic acid, a calibration curve was used. This curve was made by dissolving known amounts of the compound in Bu₄PBr, adding 1.5 mL mesitylene and 0.5 mmol tetradecane and performing a typical derivatization and extraction procedure. To quantify other compounds, the effective carbon number (ECN) was used. For a correct quantification of the yield and conversion, the stoichiometry was accounted for. For example, lactide can be converted to 2 molecules of acrylic acid. In addition, 1 equivalent of lactoyl acrylate was counted as 1 equivalent of acrylic acid and 1 of lactic acid. Lactide and the open diester of lactic acid were each counted as 2 molecules of lactic acid. Typical gas chromatograms of the samples before and after derivatization can be seen in charts S1 and S2 respectively. Unknown products were identified using gas chromatography coupled with mass spectrometry (GC-MS). The identity of each product was confirmed by comparing the retention time with that obtained for a commercial sample of the compound, and by analysis of the mass spectrum. This was performed on an Agilent 6890N GC instrument, equipped with a HP-5 MS column, coupled to a 5973N mass spectrometer.



Chart S1. Typical gas chromatogram of sample after reaction and before derivatization with annotated peaks. Reaction conditions: 0.25 mmol of lactide, 1.7 mmol Bu₄PBr, 0.025 mmol HBr (48% in water), 200 °C, N₂ atmosphere, 2h.



Chart S2. Overlay of typical gas chromatograms for sample before (black) and after derivatization (pink) with annotation of new peaks after derivatization. For the sake of simplicity and clarity, the underivatized compound is noted in this chart, while the fully trimethylsilylated product is detected. BSTFA = N,O-bis(trimethylsilyl)trifluoroacetamide Reaction conditions: 0.25 mmol of lactide, 1.7 mmol Bu₄PBr, 0.025 mmol HBr (48% in water), 200 °C, N₂ atmosphere, 2h, followed by a typical derivatization procedure.

Gas phase Fourier Transform infrared (FTIR) spectroscopy. The gas phase composition of the samples after reaction, but before derivatization was analyzed by FTIR spectroscopy. A sample of the headspace inside the vial was taken using a syringe as explained in the main text. This sample was injected through a septum into a N_2 flow which was introduced into a Gasmet DX4000 FTIR gas analyzer. The IR data were processed with Calcmet Standard software version 12.161. The software provides the volume ratios (vol% or ppm) of the different gases in the cell of the IR detector. From these results, volume percentages in the syringe and vial, and eventually reaction yields are calculated. The infrared spectrum of a typical sample is shown in Chart S3.



Chart S3. Fourier Transform infrared spectrum of a typical headspace sample. Reaction conditions: 0.25 mmol of lactide, 1.7 mmol Bu₄PBr, 0.025 mmol HBr (48% in water), 200 °C, N₂ atmosphere, 2h.

³¹P Nuclear magnetic resonance (NMR) measurements

¹H decoupled ³¹P NMR measurements were performed on a Bruker Avance 400 MHz spectrometer equipped with a BBO 5 mm atma probe and a sample case. A pulse sequence with a delay time (D1) of 5 s was used and 64 scans were recorded. The results of ³¹P NMR analysis of Bu₄PBr before and after reaction in d-DMSO are shown in Chart S4. For both samples the only significant peak corresponds to Bu₄PBr.²



Chart S4. ¹H decoupled ³¹P nuclear magnetic resonance spectra of Bu₄PBr before and after reaction, top: full spectrum, bottom: magnification of relevant region. Reaction conditions: 0.25 mmol of lactide, 1.7 mmol of ionic liquid, 0.025 mmol HBr, 200 °C, N₂ atmosphere, 2h.

Comparison of different lactic acid based substrates

Different substrates related to lactic acid were tested (Chart S5). As explained in the manuscript, if AA is detected, it is also detected as its ester with LA and the yields of these two products are summed as the total acrylic acid yield. Furthermore, lactic acid is also detected as its open dimeric ester, as lactide and in 2-acryloyl lactic acid. These four compounds are grouped as unconverted lactic acid. Using a 90 wt% aqueous solution of lactic acid results in a 18% yield of acrylic acid (AA) after 2 hours (Chart S5).

In the reaction of methyl lactate, the ester bond of part of the substrate is either hydrolyzed or cleaved by protonation and nucleophilic attack of bromide. The resulting methanol or methyl bromide reacts with the hydroxyl group of methyl lactate or lactic acid, forming methyl 2-methoxypropionate or 2-methoxypropanoic acid respectively. As a result, acrylic acid and lactic acid are detected in a larger number of different forms than in the reactions of lactic acid and lactide. For clarity, the yields of methyl acrylate, acrylic acid and the ester of lactic and acrylic acid are summed as the total acrylic acid yield. The unconverted methyl lactate consists of methyl lactate itself, lactic acid, the open dimer of lactic acid, lactide, 2-methoxypropanoic acid and methyl 2-methoxypropionate. In this reaction, a low total AA yield of 5% is achieved. This can be explained by the *O*-methylation of the hydroxyl groups. As a result, part of the initial hydroxyl groups are protected from dehydration.

Another potential substrate is calcium lactate, the form in which lactic acid is generally obtained from fermentation. After the reaction, but before derivatization, 0.6 mmol of H_2SO_4 was added to protonate the carboxylate groups. However, no lactate was converted and no acrylic acid or acrylate was formed. This can be explained by the basicity of calcium lactate. Because of this basicity, lactate neutralizes the acid cocatalyst that is required in the reaction and therefore, no reaction occurs. Finally, the highest yield by far was achieved using DL-lactide as substrate.



Chart S5. Conversion of different substrates and yield of major products in Bu_4PBr with added HBr. Conditions: 0.25 mmol of lactide or 0.5 mmol of other substrate, 1.7 mmol of Bu_4PBr , 0.025 mmol of HBr, 200 °C, N_2 atmosphere, 2h.

Effect of H₂SO₄ content

Using no or only 1% H₂SO₄ results in a low acrylic acid yield and formation of 2,3-pentanedione (Chart S6). On the other hand, 5% H₂SO₄ leads to high ethylene formation. The best selectivity is reached at an intermediate H₂SO₄ content, 2.5 mol%.





References

- (1) Stalpaert, M.; Cirujano, F. G.; De Vos, D. E. ACS Catal. 2017, 7, 5802–5809.
- (2) Bio-Rad Laboratories, Inc. SpectraBase; Compound=7rF0Wy26GOz Spectrum=1KdhjdCm4OO,

http://spectrabase.com/spectrum/1KdhjdCm4OO (accessed January 2018).