Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Local reactivity descriptors to decipher the electrochemical hydrogenation of unsaturated carboxylic acids†

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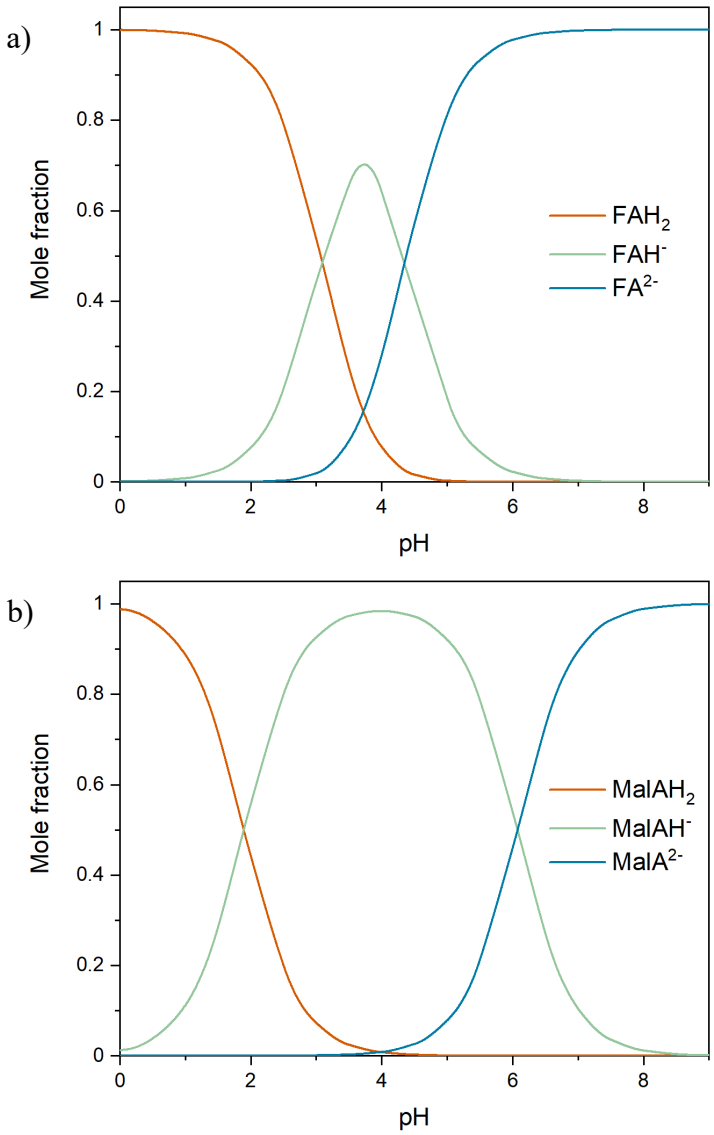

Figure S1. Speciation diagrams for (a) fumaric acid (pKa_1=3.03 and pKa_2=4.57), and (b) maleic acid (pKa_1=1.9 and pKa_2=6.07). The diagrams show the relative abundance of the diprotic, monoprotic, and fully deprotonated species.

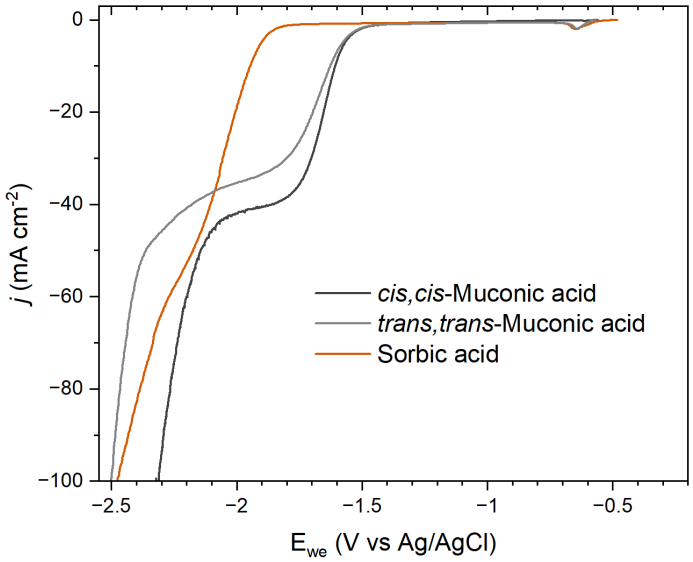

Figure S2. Current-potential polarization curves on Pb RDE for 5 g/L solutions of *cis,cis*-muconic acid, *trans,trans*-muconic acid, and sorbic acid at pH 7. The two isomers show the same onset potential for the hydrogenation reaction at -1.55 V while the onset is shifted to -1.90 V for sorbic acid.

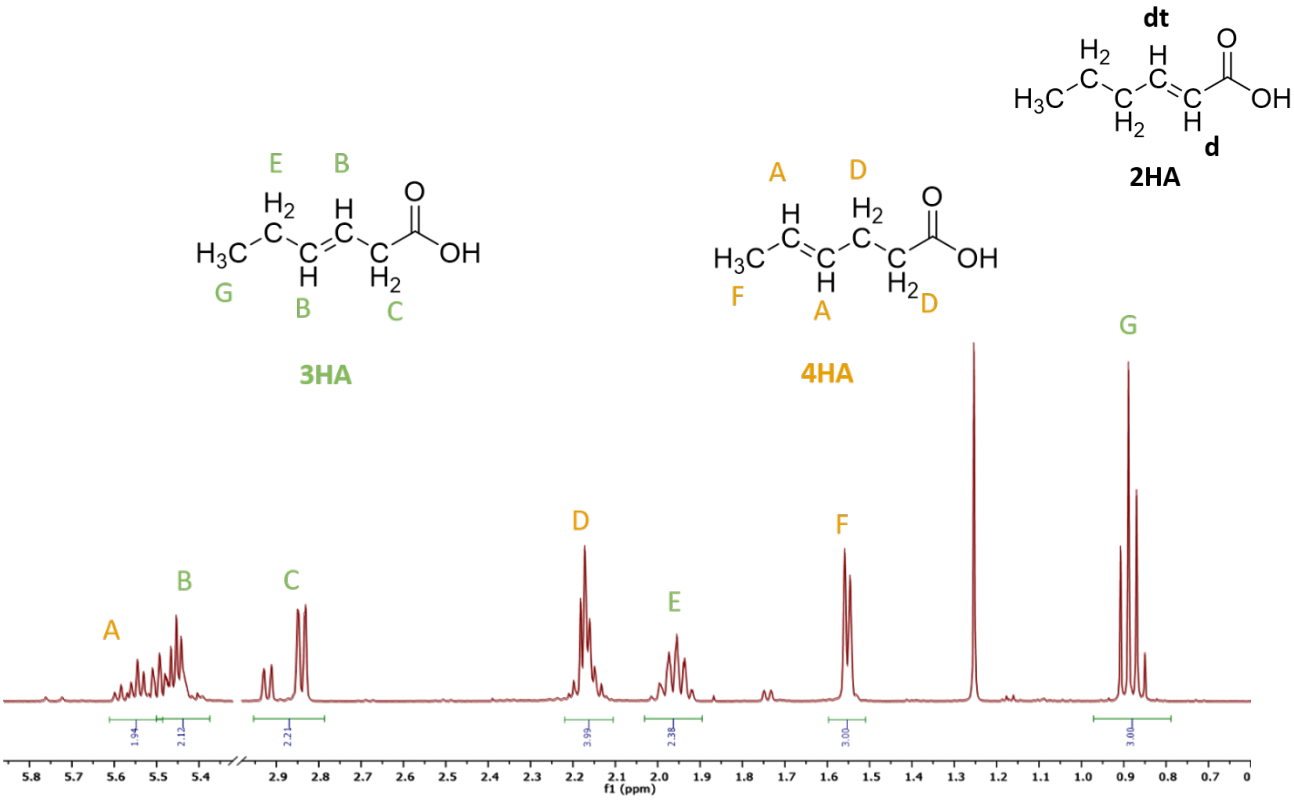

Figure S3. ^{1}H NMR spectrum of the solution collected after bulk electrolysis of sorbic acid. The products were identified and quantified by following the criteria of splitting (n+1 rule), integration, and chemical shift. **3HA:** B δ 5.43 ppm (m, 2H), C δ 2.84 ppm (d, J = 6.8 Hz, 2H), E δ 1.96 ppm (p, J = 7.4, 6.9 Hz, 2H), G δ 0.88 ppm (t, J = 7.7 Hz, 3H). **4HA:** A δ 5.55 ppm (m, 2H), D δ 2.17 ppm (hept, J = 6.3, 4.8, 4.3, 4.2 Hz, 4H), F δ 1.55 ppm (d, J = 5.0 Hz, 3H). **2HA** was not detected as it would have shown two distinctive peaks in the olefin region, δ 5.9 ppm (d, J = 15.7 Hz, 1H), δ 7.15 ppm (dt, J = 15.7, 6.8 Hz, 1H). Such peaks are absent in the spectrum.

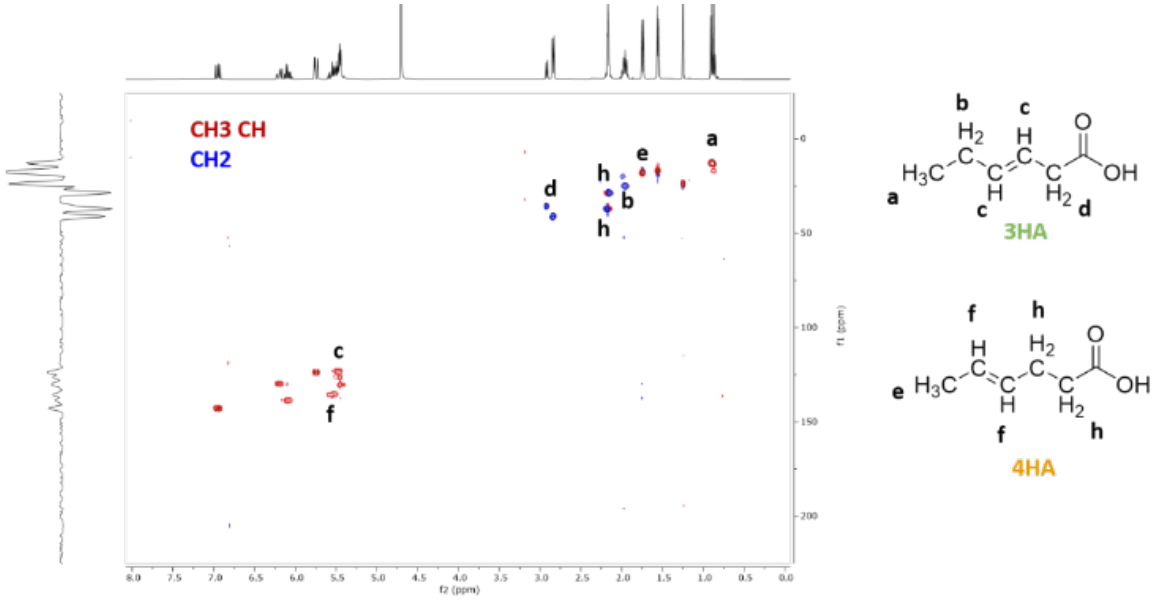

Figure S4. NMR HSQC spectrum of the solution collected after bulk electrolysis of sorbic acid. CH2 groups and CH3/CH groups appear in blue and red, respectively.

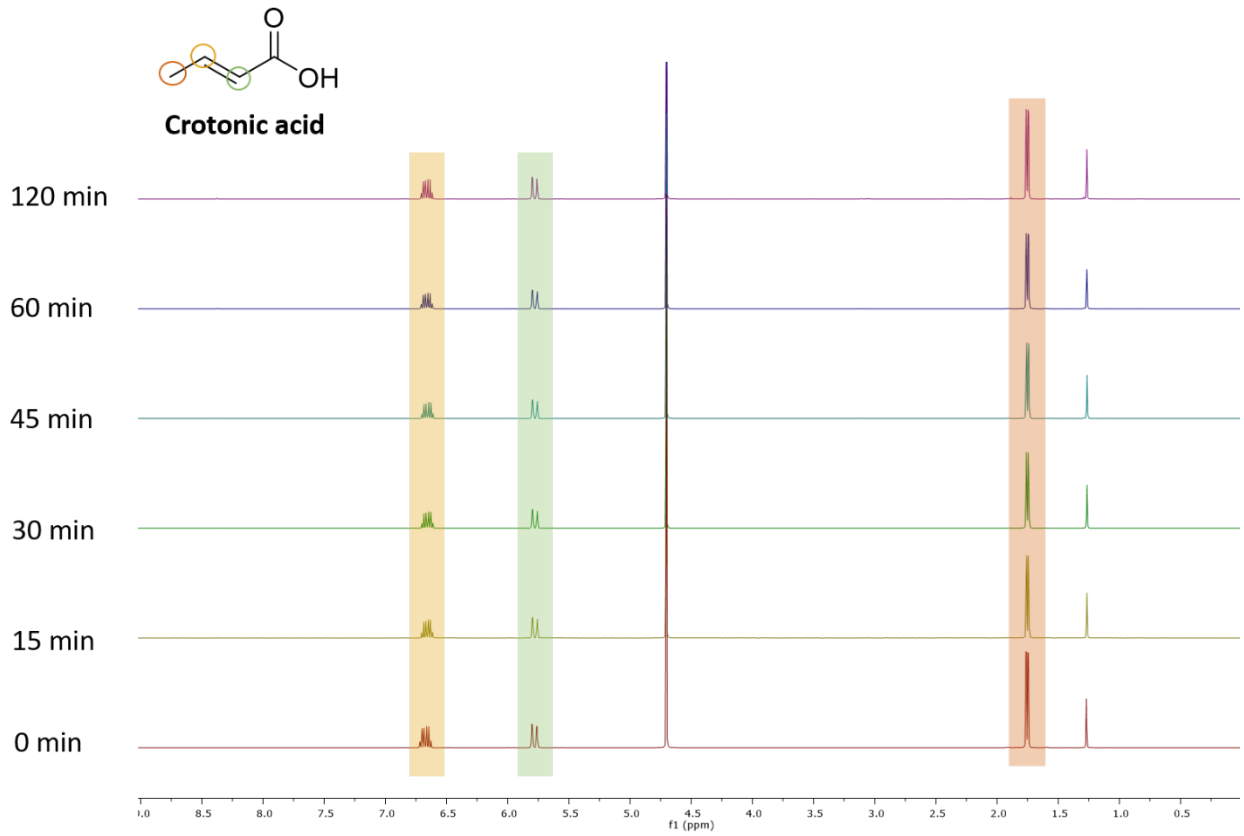

Figure S5. ^{1}H NMR spectra collected during bulk electrolysis of crotonic acid at constant current (200 mA cm^{-2}). No products could be detected during the 2-hour reaction.

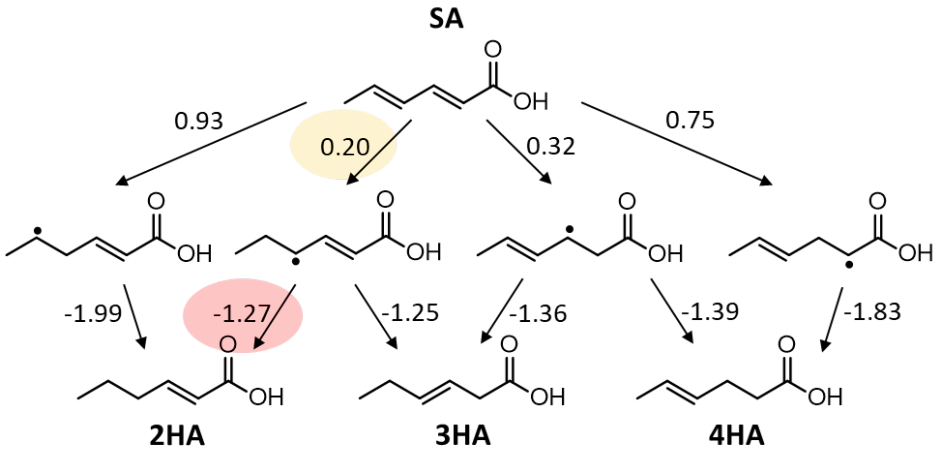

Figure S6. Changes in free energy (eV) for the sequential addition of $H^+|e^-$ pairs to sorbic acid (SA) to form the hydrogenated hexenoic acid products. Energetics are presented at -0.48 V vs. Ag/AgCl for consistency with Fig. 1 of the main text. Following the minimum-energy pathway does not predict the experimental product distribution.

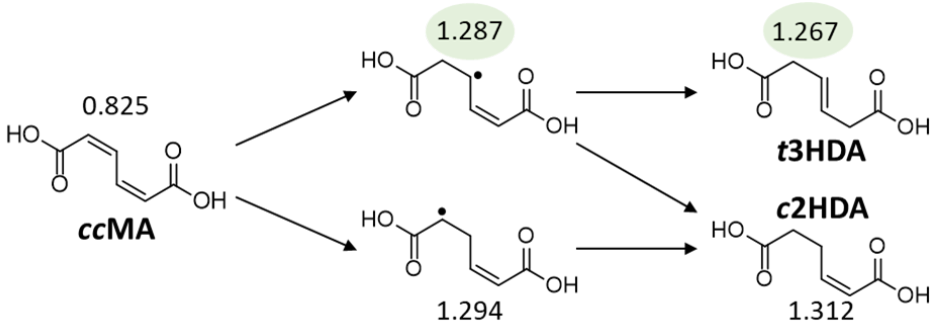

Figure S7. LUMO energies (eV) of species involved in *cis,cis*-muconic acid (*cc*MA) electrohydrogenation to hexenedioic acid products. The species with the lowest LUMO energies are those observed experimentally.

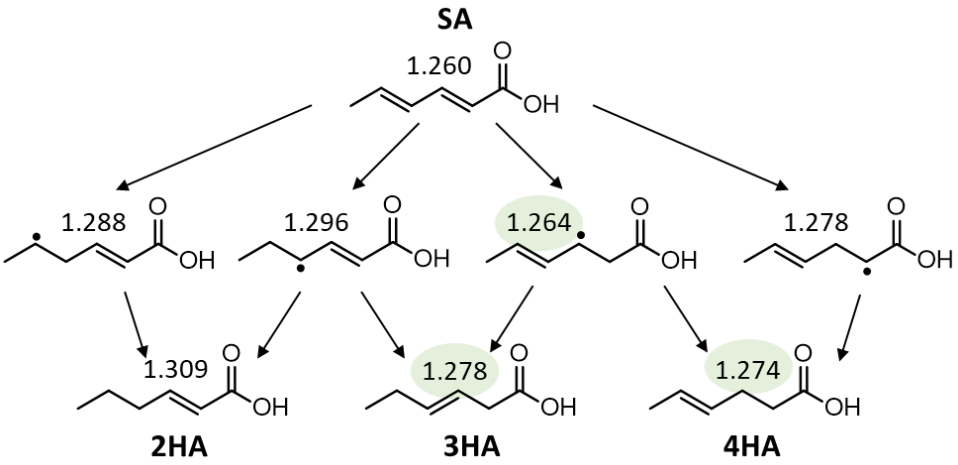

Figure S8. LUMO energies (eV) of species involved in sorbic acid (SA) electrohydrogenation to hexenoic acid products. The species with the lowest LUMO energies are those observed experimentally.

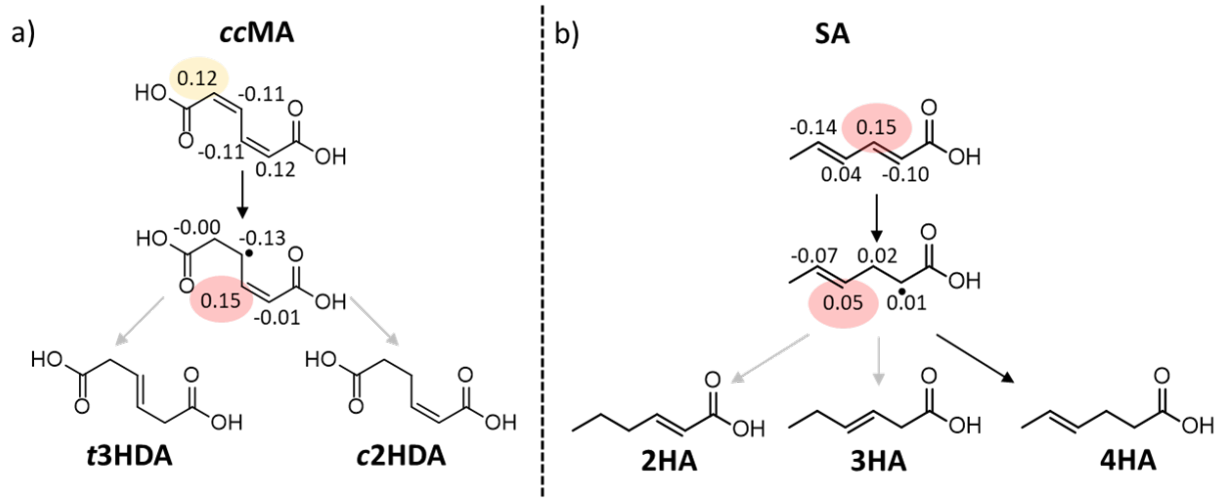

Figure S9. LUMO coefficients (given by $2p_z$ eigenvalues) of (a) *cis,cis*-muconic acid (*cc*MA) and (b) sorbic acid (SA). Included are the intermediates formed by hydrogenation at the 2pz-predicted most favorable sites (yellow).