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Supplementary Information:

On the role of C₄ and C₅ products in electrochemical CO₂ reduction via copper-based catalysts

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A Electrochemistry measurements

During the experiments, the potential applied against the Hg/HgO the reference electrode was controlled and current measured. For better comparison, we convert all voltages to reference other standards: First we convert to Standard Hydrogen Electrode (SHE) and then to the pH-independent Reversible Hydrogen Electrode (RHE) as follows:

$$U_{\rm SHE} = U_{\rm Hg/HgO} + 0.098\,\rm V \tag{A.1}$$

$$U_{\rm RHE} = U_{\rm SHE} + 0.828\,\rm V \tag{A.2}$$

Before the GC-MS measurements were conducted, a Frequency Response Analysis (FRA) was carried out to determine the internal resistance for iR compensation, see Fig. S1. At high frequencies, the Faradaic resistance of the electrode-electrolyte interface drops to zero because of the double-layer capacitance. At this point, the imaginary part of the impedance is gone and we get $R_i = \Re(Z_0)$ with $\Im(Z_0) \approx 0$.



Figure S1: Complex impedance measured in FRA.

It is best practice to multiply with a correction factor of 0.7 [1], so we get

$$R_i = \Re(Z_0) \cdot 0.7 = 1.981\,\Omega\tag{A.3}$$

The final iR compensation is then applied via

$$U_{\text{RHE}}^{\text{corr}} = U_{\text{RHE}} - J_{\text{total}} \cdot R_i + \frac{RT}{F} \ln(10) \cdot \text{pH}$$
(A.4)

with the assumption of pH = 14. Relevant values are given in Tab. S1.

	time			Appli	ed potenti	al [mV]		
	time	2000	2500	3000	3500	4000	4500	5000
	5 min	-2000	-2500	-3001	-3501	-4000	-4500	-4999
$U_{ m Hg/HgO}$	30 min	-2000	-2501	-3001	-3500	-4000	-4500	-4998
	average	-2000	-2501	-3001	-3500	-4000	-4500	-4999
	5 min	-188	-405	-523	-762	-922	-1003	-1624
$J_{\text{total}} \left[\frac{\text{mA}}{\text{cm}^2} \right]$	30 min	-190	-417	-554	-786	-901	-1049	-1702
	average	-189	-414	-541	-760	-909	-1054	-1654
	5 min	-1902	-2402	-2903	-3403	-3902	-4402	-4901
$U_{ m SHE}$	30 min	-1902	-2403	-2903	-3402	-3902	-4402	-4900
	average	-1902	-2403	-2903	-3402	-3902	-4402	-4901
	5 min	-1073	-1574	-2075	-2575	-3074	-3573	-4073
$U_{ m RHE}$	30 min	-1074	-1575	-2075	-2574	-3074	-3573	-4072
	average	-1074	-1574	-2075	-2574	-3074	-3573	-4073
	5 min	-701	-772	-1038	-1065	-1247	-1586	-855
$U_{ m RHE}^{ m corr}$	30 min	-697	-749	-979	-1016	-1289	-1494	-701
	average	-700	-755	-1004	-1069	-1273	-1486	-797

Table S1: Conversion and compensation of applied potential during the measurements.

As we can see in Fig. S2, the absolute compensated applied potential vs. RHE seems to decrease while the uncorrected applied potential is increased. The reasons are probably that internal surface area has increased by wetting/restructuring and/or decrease of iR. This is supported stark by drop in CO_2 and H_2CO_3 registered for the largest current which indicates a high CO2R rate. There is probably also lots of hydrogen being produced.



Figure S2: Converted and compensated applied potential values.

B Gas Chromatography

The exhaust of flow cell was directed into the sampling loop of an Agilent 7890 gas chromatograph (GC). Packed column Hayesep D was used to separate products. In order to extract also products that would take an impractical large amount of time to elute from the column, it was heated up in two steps, see appendix B.1. For the species identification, we rely on some well-known (relative) retention times for this specific column, see B.2. These can be put into absolutes and compared to species found.

B.1 Heating procedure

The heating protocol of the column started off at $T_1 = 70$ °C which was held for 3 min. A first heating ramped followed with a rate of 40 °C min⁻¹ until $T_2 = 125$ °C was reached and held again for 2 min. A final rate with the same rate of 40 °C min⁻¹ brought the temperature up to a final $T_3 = 200$ °C which was held for 40 min until the end of the experiment.

Fig. S3 shows the temperature curve. The first heating ramp starts after $t_{1A} = 180 \text{ s} = 3 \text{ min}$ and ends after $t_{1B} = 262.5 \text{ s} = 4.375 \text{ min}$. The second heating ramp starts after $t_{2A} = 382.5 \text{ s} = 6.375 \text{ min}$ and ends after $t_{2B} = 495 \text{ s} = 8.25 \text{ min}$. Heating ends after $t_3 = 2895 \text{ s} = 48.25 \text{ min}$.



Figure S3: Heating protocol of the GC column used in the experiment.

The heating causes some of the polymers that make up the stationary phase to disintegrate so they are detected by the PTR-MS. This happens continuously it only leads to a shift

of the signals' baselines that needs to be accounted for. This is shown exemplary for the $C_3H_7O^+$ trace which exhibits a clear two-step-plateau. Start and end are marked with vertical lines at $t_1 = 3.4 \text{ min}$, $t_2 = 6.8 \text{ min}$, and $t_3 = 48 \text{ min}$. This shows that - as expected - the heating leads to an increase in detected counts per second with a slight delay of a few seconds.



Figure S4: *Signals for* $C_3H_7O^+$ *trace* (m/z = 59.05 Da).

These baseline plateaus need to be accounted for in data processing as explained in section C.3. We were able to confirm their origin and intensity levels by comparison to reference experiments as detailed in section F.2.

B.2 Documented retention times

Estimated (relative) retention times for the Hayesep D column are based on manufacturer information and published chromatograms listed below.

- 1. https://www.vici.com/columns/r-index-d.php [2]
- 2. https://www.vici.com/hayesep/rettimes.php [3]
- 3. https://www.vici.com/hayesep/hsd_c11.php[4]
- 4. https://www.vici.com/columns/d-mix.php [5]

The first listed reference contains the most data and is used as a reference for all the others. In order to compare retention times across different sources (therefore experimental conditions like temperature and carrier gas), a calibration is necessary. Data from the three other sources was adjusted by picking two respective species that are also part of the first (or another already adjusted) data set and making sure their values match without violating relative retention times within a data set. Tab. S2 shows documented (i.e. value read from table or diagram) and adjusted values.

Table S2: Relative retention times of different hydrocarbons for Hayesep D column compiled and adjusted from different sources, all given in seconds for better distinction. Documented values ("doc.") are taken from tables or read from diagrams in respective sources listed above. For the adjusted values ("adj."), two species highlighted in yellow are chosen for which adjusted values from another source are available and all values from this source are linearly adjusted (first species used to fix intersection, the second for the slope).

J	Source 1	Sour	ce 2	Sour	rce 3	Sour	ce 4	
compound	doc.	doc.	adj.	doc.	adj.	doc.	adj.	result
hydrogen						95	89	89
methane	100	102	100			107	100	100
air		54	88					88
acetylene	180			101	154			154 to 180
ethylene	184	366	166	113	166			166 to 184
carbon dioxide		186	121			132	122	121 to 122
acetylene		348	161					161
ethane	200	504	200					200
methanol	284							284
propylene	290			235	290			290
propane	300							300
propadiene								
propyne	304							304
acetaldehyde	335							335
isobutane	381							381
1-butene	389			347	404			389 to 404
1,3-butadiene	390							390
butane	400							400
trans-2-butene	400							400
acetonitrile	403							403
cis-2-butene	404							404
acetone	441							441
methylene chloride	451							451
isopentane	485							485
carbon monoxide						99	93	93
pentane	500							500
water		516	203					203
1-pentene				518	578			578
1-hexene				836	901			901
chloroform	543							543
ethyl acetate	560							560

B.3 Absolute retention times

To help with species identification, the relative retention times compiled in appendix B.2 need to be adjusted to fit the experimental conditions at hand. This is done for the three different temperatures of the heating protocol discussed in appendix B.1. For each, a reference species is chosen the existence of which is certain: methane, ethylene, propylene. In Tab. S3 the adjusted values are shown for each regime and compared to the retention times measured in our experiment - in reality of course these values have partially helped to actually identify these species as discussed in appendix D.

1	documented	adjust	ed to ten	nperature	experiment
compound	see Tab. S2	T_1	T_2	T_3	$U_{\rm Hg/HgO} = 3 \rm V$
air	88	152	179	166	
hydrogen	89	155			
carbon monoxide	93	160			132
methane	99	172			173
carbon dioxide	121	209	246	228	231
acetylene	154	267	314		
acetylene	159	275	324		
ethylene	166	287	304		338
ethane	200	346	407		
water	203	351	413	384	
methanol	284	491		536	425
propylene	290	502		548	548
propane	300	519		567	
propyne	304	526		574	
acetaldehyde	335	580		633	628
propadiene	354	612		668	
isobutane	381	659		720	
1-butene	389	673		735	720
1,3-butadiene	390	675		737	730
butane	400	692		756	
trans-2-butene	400	692		756	744
cis-2-butene	404	699		764	761
acetone	441	763		833	918
isopentane	485	839		916	
pentane	500	865		945	
ethyl acetate	560	969		1059	1397
1-pentene	578	1000		1092	1026
1-hexene	901	1559	1835	1703	

Table S3: Documented, adjusted, and measured retention times of relevant hydrocarbons,all given in seconds for better distinction. For each section of the heatingprotocol, a calibration was made to fit a reference species highlighted in yellow.

C Methodology

Large amounts of data are generated during the experiment by the PTR-MS: Every second of the experiment, counts for specific masses are registered and saved. These need to be assigned to traces that can be then used for species identification and analysis. In total, three main steps are necessary to identify species, isolate data associated with them and calculate indicative measures for these species that can be displayed for the different applied potentials:

- 1. Separation and export of traces
- 2. Assignment of traces and identification of species
- 3. Deconvolution of species' traces and data analysis

The workflow is illustrated in Fig. S5: A 3-dimensional data set (for each measurement) is first broken down into a number of discrete 2-dimensional data sets, see appendix C.1. These are then split into smaller 2-dimensional data sets (along the time dimension) and assigned to groups (species), see appendix C.3. Some post-processing is done to each data set of each group to produce some measure of concentration or isotope fraction that can be compared to the same measure from other experiments (or even other groups), see appendix C.3.



Figure S5: General workflow of data analysis for GC-MS experiments conducted.

C.1 Separation and Export

Original PTR-TOF-MS data was collected in cycles of 1 s where detector signal was averaged for each cycle period and recorded into a file. Consecutive collection of cycles was further evaluated with the PTRMS Viewer software [6] in order to extract intensities of each trace over time. Peaks were fitted with Pseudo-Vougt function as it found to be most accurate in simulating its areas. For the 7 main measurements conducted, 75 traces were exported for further analysis. They are listed in Tab. S4 with their masses and the ion the trace was based on. Each of them was selected for at least one of the following reasons:

- Clear peak was detected
- Known ionization product of common hydrocarbon
- Isotope of trace with large signal
- · Keeping track of primary ions and water clusters

It is important to keep in mind that the traces will inevitably also include signals of other ions with very similar masses. For example, the difference in mass between an an additional hydrogen atom and an additional neutron in one of the carbon atoms is $\approx 0.002 \text{ Da}$ and therefore beyond the resolution of our PTR-MS. Furthermore, shifting baseline signals due to GC heating (see appendix B.1) were observed for a majority of traces.

This is related to the reason why we did not use an available software tool such as AMDIS for signal deconvolution and product identification. First of all, there is no extensive PTR-TOF-MS database available. Furthermore, deconvolution needs to be done differently as overlaps are observed on the mass as well as the time axis and while the TOF sensor can actually discriminate between ions of very similar atomic mass units. Deconvolution of different traces at similar times is not the main issue here but rather that of the same or similar (overlapping) traces at similar times. Lastly, the subtraction of complex rising and falling baselines due to GC heating other systemic effects needed to be done manually.

C.2 Species Identification

After exporting the traces, their signals were analysed and peaks detected in an automated fashion. For this, the signal data was smoothed by a moving average with a window length of $\Delta t = 10$ s. The derivative of the smoothed signal was then approximated by the difference quotient. Based on detected baseline noise levels (via median signal values and derivatives), different thresholds for smoothed signal and derivative were set as shown in Fig. S6. When certain conditions were met, a peak was identified. For peak location the time with the maximum smoothed signal value was chosen, peak boundaries were set at the times signal and derivative fell below defined thresholds again.

The example trace in Fig. S6 exhibits two plateaus due to GC heating as described in B.1. For the peaks on different baselines, the signals can be separated into different temperature regimes and re-processed separately if peak detection is unclear - which is not the case

Table S4: List of all exported traces with their mass-to-charge ratio and the composition
of the ion this export was based on. Formulas refer to the most common iso-
topes if not specified otherwise - then the exception applies to one of the atoms.
All traces with signal plateaus due to GC heating are highlighted, minor base-
line shifts in green and major ones in yellow.

m/z[Da]	trace	m/z [Da]	trace	m/z [Da]	trace
21.022	$H_{3}O^{+}(O_{18})$	46.037	$C_{2}H_{5}O^{+}(C_{13})$	73.028	$C_3H_5O_2^+$
26.016	$C_2H_2^+$	47.013	$\mathrm{CH_{3}O_{2}^{+}}$	73.066	$C_4H_9O^+$
27.023	$C_2H_3^+$	47.049	$C_2H_7O^+$	77.060	$C_3H_9O_2^+$
28.032	$\mathrm{C_{2}H_{4}^{+}}$	48.052	$C_{2}H_{7}O^{+}\left(C_{13}\right)$	78.063	$C_{3}H_{9}O_{2}^{+}(C_{13})$
29.039	$\mathrm{C_{2}H_{5}^{+}}$	53.040	$\mathrm{C_4H_5}^+$	79.039	$\mathrm{C_{2}H_{7}O_{3}^{+}}$
31.018	$C_2H_6^+$	55.038	$H_7O_3^+$	79.056	$C_6H_7^+$
31.019	$C_2H_3O^+$	55.055	$C_4H_7^+$	79.075	$C_{3}H_{11}O_{2}^{+}$
33.033	$C_2H_5O^+$	57.070	$C_4H_9^+$	83.049	$C_5H_7O^+$
33.994	$O_2^+(O_{18})$	58.041	$C_3H_6O^+$	83.086	$C_{6}H_{11}^{+}$
34.037	$CH_{5}O^{+}(C_{13})$	59.050	$C_3H_7O^+$	85.028	$C_4H_5O_2^+$
37.028	$H_5O_2^+$	60.052	$C_{3}H_{7}O^{+}(C_{13})$	86.036	$\mathrm{C_4H_6O_2^+}$
39.025	$C_3H_3^+$	61.029	$\mathrm{C_{2}H_{5}O_{2}^{+}}$	87.045	$\mathrm{C_4H_7O_2^+}$
40.031	$C_3H_4^+$	61.065	$C_3H_9O^+$	89.058	$C_4H_9O_2^+$
41.039	$C_3H_5^+$	63.044	$\mathrm{C_{2}H_{7}O_{2}^{+}}$	91.083	$C_4H_{11}O_2^+$
42.042	$C_3H_6^+$	63.008	$CH_3O_3^+$	93.070	$C_7H_9^+$
43.018	$C_2H_3O^+$	64.047	$C_2H_7O_2^+(C_{13})$	97.101	$C_{7}H_{13}^{+}$
43.055	$C_3H_7^+$	64.011	$CH_{3}O_{3}^{+}(C_{13})$	101.060	$C_5H_9O_2^+$
43.989	$\mathrm{CO_2}^+$	65.061	$\mathrm{C_{2}H_{9}O_{2}^{+}}$	103.075	$C_{5}H_{11}O_{2}^{+}$
44.021	$C_{2}H_{3}O^{+}\left(C_{13}\right)$	66.063	$C_{2}H_{9}O_{2}^{+}(C_{13})$	105.091	${\rm C_{5}H_{13}O_{2}^{+}}$
44.058	$C_{3}H_{7}^{+}(C_{13})$	67.054	$C_4H_3O^+$	107.070	$C_4H_{11}O_3^+$
<mark>44.99</mark> 8	$\rm CO_2 H^+$	69.069	$C_5H_9^+$	107.088	$C_8H_{11}^+$
45.033	$C_2H_5O^+$	71.049	$C_4H_7O^+$	119.086	$C_9H_{11}^+$
46.000	$CO_{2}H^{+}\left(C_{13}\right)$	71.086	$C_5H_{11}^+$		

here. Location of peaks and plateaus can be double-checked manually by looking at cumulated signal counts - jumps constitute peaks and constant slopes constitute plateaus.

All detected peaks of all recorded traces were then clustered according to the time of peak signal. A few notable time ranges emerged where for many traces peaks were recorded for all applied potentials. For some other time ranges, only few peaks were recorded at only some of the applied potentials. After elimination of some measurement artefacts, all these time ranges correspond with one or more detected species.



Figure S6: Exemplary peak detection for $C_3H_5^+$ trace at $U_{Hg/HgO} = 3500 \text{ mV}$, all figures show experimental time in seconds on the x-axis. The top figure shows the smoothed signal data in pink and its derivative in blue. The left y-axis refers to the signal data and the green horizontal indicates the detected baseline signal. The right y-axis refers to the derivative and the red horizontal lines indicate expected noise boundaries. The detected peaks are numbered from 1-4 and their detected boundaries are indicated by black vertical lines. The bottom left figure shows raw signals and their values from integration over the detected boundaries. The bottom right figure shows the cumulated signal sum compared to individual peak contributions.

These species are most likely products of the electrocatalytic reduction of carbon dioxide and were identified (see appendix D) via one or multiple of these three benchmarks:

- 1. Comparison of the time at which a peak was detected to GC retention times given by the manufacturer (compiled and adjusted, see appendix B.3) or verified by us with pure substances
- 2. Comparison of traces peaking at the same time and their signal ratios with expected ions and fragments according to SIFT studies (see appendix E.1.2) or from analogy to similar species
- 3. Relative intensities of traces across applied potentials (compared to known species in existing literature, e.g. [7])

C.3 Species Analysis

After assigning all peaks of all traces to certain species (or times), the signals are integrated within the determined boundaries of their peak. This integration is partially done already as part of the species identification process described in C.2 but re-done for the quantitative analysis. For a better separation of peaks as well as precise determination of peak time, signals are first smoothed via moving average as described before. The detected baseline is subtracted from the signal subsequently, which not only helps remove systematic errors (e.g. polymer disintegration from GC heating) but also separation of overlapping signals of species with similar elution times. For this reason, the underlying baseline was assumed to be a quadratic function from the boundary with the smaller signal value to the boundary with the larger signal value which results in the subtraction of $2/3\min\left(\overline{I(t_1)},\overline{I(t_2)}\right) + 1/3\max\left(\overline{I(t_1)},\overline{I(t_2)}\right)$ from the signal within the defined boundaries t_1 and t_2 . This is a suitable assumption since it removes a plateau efficiently (subtracted value will be close to linear average) as well as it deconvolutes overlapping peaks as the arm of a Gaussian function close to the peak is approximated well by a quadratic function. In a next step the signal is integrated within these boundaries by summing up the counts recorded for every second: $\int_{t_1}^{t_2} I(t) = \sum_{j=x(t_1)}^{x(t_2)} I(x)$.

For the absolute values (counts) listed in D, we use a moving average of window length $\Delta t = 8 \text{ s}$ for the initial smoothing of the signal and an additional length $t_b = 5 \text{ s}$ for the lower and upper boundaries to compute the baseline from mean values $\overline{I(t_1)} = 1/t_b \sum_{j=x(t_1-t_b)}^{t_1} I(x)$ and $\overline{I(t_2)} = 1/t_b \sum_{j=x(t_2)}^{t_2+t_b} I(x)$. For an in-depth analysis of the data, additional post-processing is necessary to satisfy the following requirements: First of all, some measure of accuracy is needed (like standard deviation) which requires data sampling. Furthermore we need relative values so data points can be compared with one another - for this, two slightly different workflows have been established: the first in C.3.1 to calculate a relative Faradaic Efficiency for "internal" comparison (same trace or at least species across different applied potentials) and the second in C.3.2 to calculate trace fractions for "external" comparison (same applied potential across different traces or even species) and finally to compute a measure of the Kinetic Isotope Effect.

C.3.1 Measure for Faradaic efficiency

For FE we want to capture the full signal also in its width because for large concentrations peaks do not only get more intense but also broader due to the GC column. The tabulated signal integration values in D depend on the chosen parameters for post-processing, so these need to be sampled calculating a measure of accuracy. As is shown in Fig. S7, the post-processing of the signal is done many times for all possible combinations of window length for moving average, exact boundary location in relation to the detected ranges, and window length for baseline calculation at the boundaries. With over 1,000 data points generated, statistical operations can be carried out with confidence on the distribution at hand - specifically, mean and standard deviations are calculated.



Figure S7: Data analysis workflow for obtaining relative intensities across applied potentials and specifically a (relative) measure for Faradaic Efficiencies.

Since exact rate constants for the PTR reactions are unavailable (see appendix E), we cannot calculate species concentrations and therefore Faradaic Efficiencies. A few steps can be taken though to come up with at least a relative measure for Faradaic Efficiencies (rFE): First, the integrated intensities are divided by the average current density measured at the corresponding applied potential. This way, the effect of larger currents leading to larger concentrations despite sinking (or stagnant) Faradaic Efficiencies is removed and we have a measure for CO2R selectivity. In a second step, all these values are normalized by dividing through the largest $\int I/J$ as shown in Fig. S7. The resulting relative Faradaic Efficiencies now range from 0% to 100% (which is always the maximum) can now be compared between ions originating from the same species where they should exhibit similar values. The curves of different species (CO2R products) can also be compared to one another in a qualitative fashion.

C.3.2 Measure for trace ratios

In order to quantify KIE but also the product ratios of proton transfer reactions in the PTR-MS (see appendix E), fractions of trace signals need to be calculated. In this case, using the full integrated signal between the detected boundaries would introduce a larger error due to the small signal of some minor traces and related higher noise levels further away from the peak. Since the calculation of fractions within the same experiment does not depend on the full range of the signal, we can use smaller ranges by sampling boundaries close to the actual peak location as shown in Fig. S8. While the window length for moving average smoothing is set constant ($\Delta t = 8$ s, the baseline values at the boundaries used for deconvolution and noise subtraction are mean values from sampling close to the detected signal boundaries. With 1,000 integration ranges close to the peak location then being sampled and fractions of integrated signal calculated, statistical operations can be carried out with confidence on the distribution at hand - specifically, mean and standard deviations are calculated.



Figure S8: Data analysis workflow for obtaining signal ratios between fragments or isotopes and specifically a measure for the Kinetic Isotope Effect.

The Kinetic Isotope Effect can now be quantified by calculating the fraction of signal from a ¹³C isotope in relation to its corresponding ¹²C trace and comparing this fraction to the natural ¹³C abundance of 1.1125% [8]. In above Fig. S8, $n_{C,k}$ is the number of carbon atoms in the species and r_k a correction for calculating the shift caused by KIE. Details and results are give in appendix I.

D Single species discussion

In this section the identification and analysis of individual species is discussed in detail.

An overview of all peak clusters (traces with signal peaks detected at the same times) and the corresponding species (CO2R products which were subsequently identified) is given in Tab. S5. The methodology deployed for clustering and identification is described in C.2.

Retention time $\left[s\right]$	Species detected	Comment					
129 to 135	СО	Some protonation technically too small	even though proton affinity is all, see section D.1				
168 to 177	CH ₄	Proton affinity too tion D.2	small for protonation, see sec-				
234 to 242	CO_2/H_2CO_3	Some separation of bon dioxide compo	f carbonic acid into water and car- onents observable, see section D.3				
331 to 342	C_2H_4	Additional effects large concentration	and reactions observed due to n, see section D.4				
427 to 461	CH ₂ O/CH ₃ OH	Some dissolved m see section D.5	ethanol apparently not separable,				
542 to 551	C ₃ H ₆	Additional effects and reactions observed due to large concentration, see section D.6					
622 to 631	CH ₃ CHO	Additional effects and reactions observed due to large concentration, see section D.7					
709 to 722	CH ₃ CH ₂ OH	Additional effects large concentration	and reactions observed due to n, see section D.8				
716 to 754	C_4H_8/C_4H_6	But(adi)ene isomer	rs distinguishable, see section D.9				
770 to 788	$C_{3}H_{6}^{+}$?	artefact at mass 42	, see section D.10				
862 to 875	$1-C_3H_6O$	propanal	Constitutional isomers of C2460				
903 to 925	$2-C_3H_6O$	acetone	separated by GC see section D 11				
985 to 993	CH ₂ CHCH ₂ OH	allyl alcohol	separated by GC, see section D.11				
1011 to 1029	$C_{5}H_{10}$	Pentene isomers	Peaks are quite close to each				
		distinguishable?	other, hard to distinguish; see				
1027 to 1048	CH ₃ CH ₂ CH ₂ OH	n- or i-propanol?	section D.12				
1225 to 1234	$(CH_3CO)_2$	Most likely butane	dione, see section D.13				
1310 to 1320	C_4H_8O	C ₄ H ₈ O isomers dis	stinguishable, see section D.14				
1319 to 1414	CH ₃ COOC ₂ H ₅	Actual acetate dete	ected, see section D.15				
2196 to 2222	C ₅ H ₈ O ₂	2,3-pentanedione	Constitutional isomers of $C_5H_8O_2$				
2320 to 2389	$C_5H_8O_2$	2,4-pentanedione	separated by GC, see section D.16				

Table S5: All detected peak clusters of specific retention times of the GC.

Hereafter, details for each of the listed species are given. This includes a table of all expected and detected peaks across applied potentials, their retention times and integrated signal values. The upper part of these tables gives retention times of maximum signal as well as detected boundaries of the signal as described in C.2. In the lower part, all

traces with detected peaks for these retention times are listed with their integrated signal values. For these, the raw signal has been smoothed and detected baseline was already subtracted as described in C.3. If for none of the listed traces a peak was registered for a specific applied potential, no retention times are given and the integration yields zero for all traces as there are no boundaries for summation. If for only one or multiple of the traces no peak (with reasonable SNR) was detected at a specific potential, the result from integration within the defined boundaries is given but highlighted in red since the value is not meaningful.

Detected retention times are discussed in comparison to documented and expected (relative) retention times as mentioned in section B.2 and B.3. The discussions around species identification also include arguments regarding different species' proton affinities that are listed in section E.1.3 since this value indicates if we expect (substantial) protonation of a potential CO2R product or not. Furthermore, we confirmed species within and verified baseline within multiple reference experiments (including ¹³C) described in section F.

A few types of figures and graphs are deployed to support identification and analysis discussion. The most prominent ones are extracted ion chromatograms around relevant time scales, showing raw or processed signals (see section C.3) either of all relevant traces at a specific applied potential or of a specific traces signal for all applied potentials. To illustrate observed selectivity trends and potential dependence, additional graphs are shown of relative Faradaic Efficiencies (see section C.3.1) calculated with relevant traces across all applied potentials. For some of the species, we also depict show the share of integrated signal (see section C.3.2) from relevant traces across all applied potentials.

D.1 Carbon monoxide

After 129s to 134s we detect a peak of mass m = 47.013 Da, see Tab. S6.

Dot	antion time		Appli	ed poten	tial vs. H					
Keu	ention time	2000	2500	3000	3500	4000	4500	5000		
Peak time in s		129	134	131	134	-	-	-		
Sta	rt time in s	123	129	123	127	133	-	-		
End time in s		142	148	142	146	146	-	-		
m/z	Ion assumed	Inte	egrated si	noothed	intensity	(Norma	lized cou	nts)	Origin	Comments
47.01	$CO \cdot H_3O^+$	264	340	292	246	191	0	0	$CO + H_3O^+$	Proton affinity too small,
										but due to large concen-
										tration at small U _{Hg/HgO} ,
										some clusters are forming.

Table S6: All detected traces that are peaking with carbon monoxide.

We do not expect to see carbon monoxide via the PTR-MS since its proton affinity is smaller than that of water but multiple indicators point towards it. First of all, it lines up with the expected retention time of CO for this column. Second, it seems to be the trace of a cluster with H_3O^+ (rather than proton being completely transferred). Third, rFE shown in Fig. S9(b) follows the trend observed for carbon monoxide with other methods: it can only be detected for small to medium applied potentials and production peaks at a relatively small applied potential.



Figure S9: Analysis of chromatograms and peak areas related to CO.

These results were not be reproduced with ${}^{13}C$ as for the large current densities used in section F we do not expect a recognisable signal (compare to Fig. S9(a)).

D.2 Methane

At this retention time (168 s to 177 s) we expect to find methane but it also has a proton affinity much smaller than water so that it cannot be protonated by H_3O^+ . The small contamination of O_2^+ can ionize the methane though, leading to $CH_3 \cdot O_2^+$ according to [9]. But since only a small fraction of the produced methane will get ionized, we observe clustering reactions shown in Tab. S7 with the few ionized methane molecules as discussed in section E.2.

D - 4			Appli	ed poten	tial vs. H	lg/HgO i	in mV			
Reti	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	ık time in s	-	-	174	174	177	170	169		
Start time in s		-	-	165	165	169	160	160		
En	d time in s	-	-	184	184	188	179	179		
m/z	Ion assumed	egrated si	noothed	intensity	(Norma	lized cou	nts)	Origin	Comments	
47.01	$CH_3 \cdot O_2^+$	0	0	12	142	5	451	1349	$CH_4 + O_2^+$	Ionization by
										residual O_2^+ [10]
63.04	$C_2H_7O_2^+$	0	0	-5	6	6	8	8	$CH_3 \cdot O_2^+ + CH_4$	Just hypothetical
33.03	¹² CH ₅ O	0	0	1787	4646	8251	8134	7939	$C_2H_7O_2^+ - CH_2O$	Isotope ratio
34.04	¹³ CH ₅ O ⁺	0	0	25	86	99	80	96		around 1.5%
43.02	$C_2H_3O^+$	0	0	194	290	421	407	475	$C_2H_7O_2^+ - H_2 - H_2O$	
31.02	CH ₃ O ⁺	0	0	440	450	2349	3104	2567	$C_2H_7O_2^+ - CH_3OH$	Alternatively
										$CH_3O_2^+-O$

Table S7: All detected traces that are peaking with methane.

Due to the large concentration, almost all $CH_3 \cdot O_2^+$ ions cluster with unionized methane

which seems to immediate fragment mostly to CH_5O^+ which is detected as main signal (see Fig. S10(a)). For the supposed PTR reaction mechanism based on the findings, see section E.3.1. Even though the ¹³C experiment was conducted at an applied potential that would allow for considerable methane production, only a signal of CH_5O^+ with small SNR was detected. This is probably due to the fact that the electrode used was from a different batch and has therefore slightly different selectivities. The Faradaic Efficiency of methane peaked at a fairly large applied potential (see Fig. S10(b)) which is expected when considering the general trends observed in methane production. [11]



Figure S10: Analysis of chromatograms and peak areas related to CH₄.

D.3 Carbon Dioxide

For this retention time (234s to 242s) we expect to find unconverted carbon dioxide but it should not react in a significant way with any of the ionic precursors [12]. It has the lowest proton affinity of all species analysed yet but next to the CO_2^+ ionized by residual O_2^+ we actually find protonated carbon dioxide CO_2H^+ . This could be caused by the sheer number of CO_2 molecules in its large concentration, so we still see some occasional protonation. Furthermore, we detect carbonic acid which usually immediately decomposes in the gas phase. This seeming contradiction can be explained by the good solubility of carbon dioxide in water which seems to cause some of the gas phase humidity to recombine with CO_2 in the GC column. One piece of evidence indicating that detected $H_3CO_3^+$ signals are not only caused by ionization of CO_2 via a $H_5O_2^+$ is the fact that signals of water-related traces are detected as documented in Tab. S8. If we accept the existence of carbonic acid, the CO_2H^+ signal could also be caused by water dissociation from protonated carbonic acid, see Tab. S8. Signals and isotope ratios of these are quite similar (and also hard to explain if only caused by carbon dioxide) so they might be connected in this

way and carbon dioxide is not directly protonated after all.

-										
Dat	tantian tima			Applied pote	ential vs. Hg/	HgO in mV				
Ke	tention time	2000	2500	3000	3500	4000	4500	5000		
Pea	ak time in s	228	233	231	232	235	228	23		
Sta	art time in s	222	226	223	225	227	220	223		
Er	nd time in s	271	275	272	274	276	269	272		
m/z	m/z Ion assumed Integrated smoothed intensity (Normalized counts)									Comments
37.03	$H_2O \cdot H_3O^+$	1264804	1150109	1300788	1302750	1145293	1146872	995620	$H_2O + H_3O^+$	
55.04	$2H_2O \cdot H_3O^+$	6345	4920	5636	4661	5415	4268	3598	$2H_2O + H_3O^+$	signal $\approx 5\%$ of above
43.99	CO_2^+	3605	3741	3681	3502	3421	3248	2517	$CO_2 + O_2^+$	-
45.00	$^{12}CO_2H^+$	54962	56098	57828	57437	55161	52793	39338	$CO_2 + H_3O^+$	Or from H ₂ CO ₃ H ⁺ -H ₂ O
46.00	$^{13}CO_2H^+$	853	859	737	747	767	630	580		Isotope ratio around 1.4%
63.01	H2 12CO3H ⁺	46005	41957	38971	36527	34585	33026	25217	$H_2CO_3 + H_3O^+$	-
64.01	H ₂ ¹³ CO ₃ H ⁺	608	532	506	519	486	368	312		Isotope ratio around 1.5%
47.01	$H_2CO_2H^+$	1089	1037	1360	1520	1744	1494	2422	$H_2CO_3H^+ - O$	small SNR

Table S8: All detected traces that are peaking with carbon dioxide.

When looking at the trace peaks, retention times of H_2O - and CO_2 -related traces seem slightly shifted which indicates some separation by the GC column. This shift is not significant enough (see Fig. S11(a)) and trends not consistent to draw any conclusions from it. All main signals of the three components were verified within the ¹³C experiment where the shift is a bit more pronounced and the order of elution (CO₂, then H₂CO₃, then H₂O) meets expectations since water should exhibit a much longer retention time than carbon dioxide.



Figure S11: Analysis of chromatograms and peak areas related to CO₂.

As can be seen in Fig. S11(b), the relative signal (integrated counts or intensities) of all related traces with good SNR decreases consistently with larger applied potentials. This is indicating that CO_2 reduction rate is actually increasing with applied potential (and not just HER or other factors that could increase total current density, see section A) which means that there is less CO2 left after the reaction. This cannot be definitively determine as large amounts of hydrogen produced can also dilute the CO_2 concentration as discussed in section G.

D.4 Ethylene

At this retention time we expect to find ethylene. Technically, its proton affinity is also smaller than water and thus should not be protonated by hydronium ions. But since the proton affinities are very similar, protonation is actually expected and corresponding reactions are documented in the literature as well as ionization via residual O_2^+ . [10]

D				Applied pote	ential vs. Hg	/HgO in mV	r			
Ke	tention time	2000	2500	3000	3500	4000	4500	5000		
Pe	ak time in s	337	341	339	339	342	335	333		
Sta	art time in s	322	326	324	324	327	319	318		
Er	nd time in s	352	356	354	354	357	349	348		
m/z	Ion assumed		Integra	ited smoothe	d intensity (Normalized of	counts)		Origin	Comments
28.03	$C_2H_4^+$	4475	8655	8494	8331	7050	5280	6406	$C_2H_4 + O_2^+$	Ionization of ethylene via O2+ [10];
										reaction rate constant seems similar to H_3O^+ ionization since signal ra- tio around 2%, same as primary ion
26.02	$C_2H_2^+$	1464	2010	1821	1811	1837	1610	1818	$C_2H_4^+ - H_2$	contamination Dissociation of hydrogen
29.04	C ₂ H ₅ +	168077	655239	777461	838673	414534	253757	358452	$C_{2}H_{4}^{+} + H_{3}O^{+}$	Protonation via primary ion, very
	-25								-2	large signal; main H3O+ product according to [10]
27.02	$C_2H_3^+$	8078	30459	36317	39799	20703	13519	18260	$C_2H_5^+ - H_2$	Dissociation of hydrogen
57.07	$C_4H_9^+$	7208	114452	172559	212993	49352	19208	38482	$C_2H_5^+ \cdot C_2H_4$	Cluster forming
55.06	$C_4H_7^+$	1093	16993	25145	30563	7697	3029	5907	$C_4H_9^+ - H_2$	alternatively via C ₂ H ₃ ⁺ · C ₂ H ₄
53.04	$C_4H_5^+$	390	5350	7778	9176	2402	1009	1863	$C_4H_7^+ - H_2$	Dissociation of hydrogen
41.04	$^{12}C_{3}H_{5}^{+}$	16896	251220	369133	453209	110184	43613	84667	$C_4H_9^+ - CH_4$	Dissociation of methane
42.04	$^{13}C^{12}C_{2}H_{5}^{+}$	555	7696	11643	13412	3482	1416	2752		Isotope ratio stable around 3.1%
69.07	$C_5H_9^+$	458	24685	46218	63421	7477	1795	4974	$C_3H_5^+ \cdot C_2H_4$	Cluster forming
93.07	$C_7H_{13}^+$	34	22	60	9	24	29	-9	$C_5H_9^+ \cdot C_2H_4$	Only hypothetical
93.07	C7H9 ⁺	-2	29	51	67	13	20	-9	$C_7H_{13}^+ - 2H_2$	not confirmed, might also be $C_4H_{13}O_2^+$ signal via $C_2H_9O_2^+ \cdot C_2H_4$
39.03	$C_3H_3^+$	1097	8724	12038	13767	4550	2217	3428	$C_3H_5^+ - H_2$	Dissociation of hydrogen
83.09	$C_{6}H_{11}^{+}$	6	121	211	293	37	10	18	$C_4H_7^+ \cdot C_2H_4$	Cluster forming
79.05	C ₆ H ₇ ⁺	5	42	127	121	34	6	0	$C_6H_9^+ - H_2$	Dissociation of hydrogen
47.05	¹² C ₂ H ₇ O ⁺	40962	156512	187021	204251	100532	62137	86747	$C_2H_4 \cdot H_3O^+$	Second H ₃ O ⁺ product according to [10], signal 20% confirmed
48.05	¹³ C ¹² CH ₇ O ⁺	929	3619	4497	4733	2344	1458	2142		Isotope ratio reliably around 2.4%
59.05	¹² C ₃ H ₇ O ⁺	536	1019	2669	3185	3437	2220	3422	$C_4H_{11}O^+ - CH_4$	Dissociation of methane
60.05	¹³ C ¹² C ₂ H ₇ O ⁺	-55	121	137	138	139	184	189		Ratio too large for isotope, confirm- ing $C_2H_4 \cdot O_2^+$
71.09	$C_5H_{11}^+$	0	23	96	91	10	-4	-10	$C_4H_{11}O^+ \cdot C_2H_4 - CH_3OH$	Cluster forming
45.03	$C_2H_5O^+$	876	3228	3712	3928	1953	1486	1898	$C_2H_7O^+ - H_2$	Dissociation of hydrogen
43.02	$^{12}C_{2}H_{3}O^{+}$	195	531	547	655	324	293	388	$C_2H_5O^+ - H_2$	Dissociation of hydrogen
44.02	¹³ C ¹² CH ₃ O ⁺	195	492	571	629	406	259	279		Isotope ratio incalculable due to CO_2^+ overlap
65.06	$^{12}C_{2}H_{9}O_{2}^{+}$	795	3155	3453	4119	1892	1160	1656	$C_2H_4 + H_5O_2^+$	coincides with visible drop in $H_5O_2^+$
66.06	¹³ C ¹² CH ₉ O ₂ +	18	88	89	128	52	24	38		Isotope ratio stable around 2.9%
91.08	$C_4H_{11}O_2^+$	-1	2	32	61	8	-5	10	$C_2H_9O_2^+ \cdot C_2H_4 - H_2$	not confirmed
43.99	CO_2^+	241	573	632	680	497	271	330	$C_2H_4 \cdot O_2^+ - CH_4$	most likely explanation since $C_2H_4 \cdot O_2^+$ confirmed even though not documented
67.054	$C_5H_7^+$	22	1318	2523	3193	505	126	305	C5H9 ⁺ - H2	
105.09	unknown	37	297	473	666	300	167	297		origin unclear

Table S9: All detected traces that are peaking with ethylene.

Due to the large ethylene concentration, additional effects were observed: Clustering of ionized ethylene with unionized ethylene, dissociation of different small molecules to create a wide range of fragments, and detectable protonation by $H_5O_2^+$ cluster ion. For the full PTR reaction mechanism based on these findings, see section E.3.2. Key species were also verified within the ¹³C experiment. Isotope ratios of the different fragments are quite different, which can be partially explained by the different numbers of ¹³C in these ions but also seem to be caused by signal overlaps with other traces such as $C_2H_4O_2^+$ and CO_2^+ , pointing towards a $C_2H_4 \cdot O_2^+$ cluster forming. Furthermore, a trace with m/z = 105 Da has been consistently detected but couldn't be ascribed to a specific fragment.

In Fig. S12 the relative Faradaic Efficiencies computed by different traces are sorted by

the supposed initial ionization reaction. Traces based on H_3O^+ ionization consistently show the same trend of increasing ethylene production while ramping up from small applied potentials, peaking at small to medium potential before declining again. Meanwhile, traces based on O_2^+ ionization seem to peak much earlier.



Figure S12: *Relative Faradaic Efficiencies of different* C₂H₄*-related traces.*

The reason for this is the complete depletion of O_2^+ ions reacting with ethylene in concentrations as large as produced at most of the applied potentials used. The ion depletion is discussed in E.2.1 and when looking at relative signals not normalized by current in Fig. S13, most O_2^+ -related traces in Fig. S13(d) can be seen at a similar level of intensity for all $U_{Hg/HgO} \leq 2.5 \text{ V}$. The relative Faradaic Efficiencies in Fig. S12(a) exhibit a relatively flat peak for a similar reason: There is a partial depletion of H_3O^+ for medium applied potentials as discussed in E.2.1: Fig. S13(a) shows a similar level of intensities at these applied potentials, the signal at $U_{Hg/HgO} = 3.5 V$ probably not peaking as high as it could have with sufficient H_3O^+ available.



S13(c): Traces related to $C_2H_4 \cdot H_5O_2^+$ ion

S13(d): Traces related to O_2^+ ionization

Figure S13: *Relative peak areas of different* C₂H₄*-related traces.*

A few exceptions are observed: Traces representing clusters show smaller relative intensities since they require two or more ethylene molecules and thereby depend on concentration with a larger exponent, see E.2.1. This is specifically obvious in Fig. S13(a) when comparing C₂-products to C₃- and C₄-products. The same applies to C₃H₇O⁺ in Fig. S13(d) for small applied potentials. At larger applied potentials, it shows larger relative intensities than C₂ traces though. For the ¹³C isotope this can be explained by signal overlap from C₂H₄ · O₂⁺. In fact, the behaviour shown seems to be a mixture of H₃O⁺ and O₂⁺ origin. This does not explain why the ¹²C version shows a similar behaviour - even though it is not as pronounced. The reason could be signal overlap with another fragment of O₂⁺ ionization origin: for example C₂H₃ · O₂⁺ via H abstraction.

D.5 Formalin

For this retention time window (413 s to 446 s), some convoluted traces are observed. Trace analysis and experience point towards formaldehyde in addition to water and small amounts of methanol, see Fig. S14. This mixture is known as formalin and since the column used is not designed to separate these components in particular, we observe them here even though methanol and water are documented with longer retention times.



Figure S14: XICs of formalin-related signals at different applied potentials.

There seems to be some separation at least - a distinct shift of peaks is visible, see Fig. S15. We first detect a CH_5O^+ peak which is the main protonation product of methanol. [13] After this, a second CH_5O^+ peak is detected, coinciding with a CH_3O^+ peak. This could be also originate from methanol as it is one of the two documented O_2^+ products. The

signal is way larger though so it points rather towards formaldehyde.[13] It seems to be mixed with methanol which is only partially separated by the GC column. Note that this sequence is contrary to usual observation of methanol taking longer than formaldehyde as per their boiling points. The last hydrocarbon peak detected is $CH_3O_2^+$, which is ascribed to formaldehyde even though it is not documented in the literature. This can be explained by water molecules interfering with the pure protonation of formaldehyde.



Figure S15: Overview of adjusted retention times of formalin-related traces peaking.

There seems to be some separation at least, a slight shift of peaks is visible. We first detect methanol, then formaldehyde and then water - see Fig. S15. Note that this sequence is contrary to usual observation of methanol taking longer than formaldehyde in most gas chromatographs. $CH_3O_2^+$ is ascribed to formaldehyde even though it is not documented in the literature [13] [9]. It shows a flat, but stretched peak and for some applied potentials even two distinct peaks, where the first one is coinciding with CH_3O^+ and the latter one with the water-related traces. This can be explained by water molecules interfering with the pure protonation of formaldehyde, details below.

Methanol appears first. Two peaks of CH_5O^+ can be distinguished for most potentials: One earlier than CH_3O^+ (almost coinciding with CH_2O -related traces) and one coinciding with CH_3O^+ peak, indicating a partial separation from formdaldehyde.

Rete	ention time		Appli	ed poten	tial vs. H					
1000		2000	2500	3000	3500	4000	4500	5000		
Peak time in s		424	429	425	426	429	421	419		
Sta	rt time in s	418	424	417	418	423	417	413		
Ene	d time in s	429	435	428	429	434	428	424		
m/z	Ion assumed	Inte	Integrated smoothed intensity (Normalized counts) Origin							Comments
33.03	CH_5O^+	1013	1144	330	155	2191	2588	2920	$CH_3OH + H_3O^+$	Only protona-
										tion product of methanol accord- ing to [13]

Table S10: All detected traces that are peaking with CH₃OH.

As can be seen in Fig. S16(a), for applied potentials of $U_{Hg/HgO} = 3.0$ V to 3.5 V the two CH₅O⁺ are barely separated and can hardly be deconvoluted. The corresponding integrated signal values in Tab. S16 are therefore marked in yellow. Moreover, Fig. S16(b)

shows a clear trend of decreasing Faradaic Efficiencies with increasing applied potentials - the decrease is monotonous if the mentioned outliers are removed. The trace was verified in the ¹³C experiment.



 $r_{10(a)}$. Smoothed intensities of efficiency frace $r_{10(a)}$

S16(b): Relative Faradaic Efficiencies of pure CH₃OH trace

Figure S16: Analysis of chromatograms and peak areas related to CH₃OH.

Formaldehyde appears second. The main signal is of directly protonated formaldehyde as its proton affinity is larger than water. A second peak of methanol coincides, see Tab. S11.

Retention time			App	lied poten						
		2000	2500	3000	3500	4000	4500	5000		
Peak time in s		431	437	431	431	436	429	428		
Start time in s		413	419	413	415	420	411	412		
End time in s		464	470	464	466	471	462	463		
m/z	Ion assumed	I	Integrated smoothed intensity (Normalized counts)						Origin	Comments
31.02	CH ₃ O ⁺	207000	20103	25575	30742	33735	31164	36007	$CH_2O + H_3O^+$	Only protonation product accord- ing to [9]
33.03	$^{12}CH_{5}O^{+}$	2682	2311	3675	3860	2011	1796	1777	$CH_3OH + H_3O^+$	see Tab. S10
34.04	¹³ CH ₅ O ⁺	34	18	43	50	32	11	12		Isotope ratio of both peaks $\approx 1\%$

Table S11: All detected traces that are peaking with formaldehyde.

As seen in Fig. S17(a) the amount of formaldehyde detected decreases steadily with applied potential as does methanol. Due to incomplete separation these signals are dependent on each other but the pure methanol signal shown in Fig. S16(b) shows a similar trend.



Figure S17: Relative Faradaic Efficiencies of traces related to formaldehyde.

Because the retention time of formaldehyde coincides with the second heating phase of the GC column, intensity baselines appear quite large. For this reason - and also due to difficult signal deconvolution - all standard deviations shown are quite large.

Water appears last. With it, a $CH_3O_2^+$ signal appears - probably due to incomplete separation from formaldehyde. The shift towards later retention times makes sense when comparing literature values and boiling points, see Tab. S12.

Retention time			A	pplied pote						
		2000	2500	3000	3500	4000	4500	5000		
Peak time in s		438	445	438	439	448	436	436		
Start time in s		432	435	431	429	438	430	427		
End time in s		457	460	456	454	463	455	452		
m/z Ion assumed			Integrate	d smoothe	d intensity (Normalized	d counts)		Origin	Comments
37.03	$H_5O_2^+$	288236	116841	264798	287558	241115	276788	223423	$H_2O \cdot H_3O^+$	
47.01	CH ₃ O ₂ ⁺	193	231	473	629	1340	1475	3230	$CH_3O^+ \cdot H_2O - H_2$	
55.04	H ₇ O ₃ +	992	908	1411	1429	915	1033	511	$2H_2O\cdotH_3O^+$	

Table S12: All detected traces that are peaking with formaldehyde-related water.

In Fig. S17(b) the relative Faradaic Efficiencies of water-related traces of formaldehyde show a similar trend than the methanol-related ones. In contrast, however, the $CH_3O_2^+$ trace exhibits an opposite trend of increasing Faradaic Efficiencies with applied potential. This might be casued by small SNR of this trace but could also point towards the actual trend for formaldehyde since all other traces analysed either show some overlap with methanol (and therefore are influenced by its trend of large Faradaic Efficiencies at small applied potentials [11]) or are water- (resp. H_3O^+ -) related and largely influenced by column heating.

D.6 Propylene

At this retention time (542s to 551s) we expect to find propylene. We expect mostly protonation by H_3O^+ as well as some ionization via residual O_2^+ [10].

				Applied pote	ntial vs. Hg/H	IgO in mV				
Retention time		2000	2500	3000	3500	4000	4500	5000		
Peak time in s		547	550	549	550	552	544	542	1	
Sta	art time in s	532	537	536	535	539	530	528		
Er	nd time in s	562	567	566	565	569	560	558		
m/z	Ion assumed		Integr	ated smoothed	d intensity (No	ormalized co	unts)		Origin	Comments
43.06	$^{12}C_{3}H_{7}^{+}$	435480	1427939	1309573	1284908	339875	204422	239703	$C_{3}H_{6} + H_{3}O^{+}$	Main product of propylene protona-
										tion according to [10]
44.06	$^{13}C^{12}C_{2}H_{7}^{+}$	12630	44081	40767	39083	10186	6154	7435		Very stable isotope ratio at 3.0%
27.02	$C_{2}H_{3}^{+}$	1257	4502	4473	4352	1069	768	872	$C_{3}H_{7}^{+} - CH_{4}$	Dissociation of methane
41.04	$^{12}C_{3}H_{5}^{+}$	80488	283117	261040	250610	64201	38970	44468	$C_{3}H_{7}^{+} - H_{2}$	Dissociation of hydrogen
42.04	$^{13}C^{12}C_{2}H_{5}^{+}$	2451	9043	8463	8164	2157	1315	1474		Isotope ratio $\approx 3.2\%$ indicates that $\approx 5\%$ are $C_2 H_c^+ \chi i_2 O_2^+ [10]$
83.09	CeHu+	86	661	634	550	108	77	21	$C_2H_5^+$, C_2H_6	Cluster forming
39.03	$C_{2}H_{2}^{+}$	2049	6889	6947	6523	1855	721	1054	$C_{2}H_{5}^{+} - H_{2}$	Alternatively $C_6H_{11}^+ - C_2H_8$
55.06	$C_4H_7^+$	196	2075	1844	1815	192	197	154	$C_6H_{11}^+ - C_2H_4$	Dissociation of ethylene
53.04	$C_4H_5^+$	14	28	35	34	17	7	2	$C_4H_7^+ - H_2$	Dissociation of hydrogen
61.07	C ₃ H ₉ O ⁺	216	706	686	580	145	94	132	$C_3H_6 \cdot H_3O^+$	Second H ₃ O ⁺ product, not docu-
										mented by [10]
43.02	$^{12}C_{2}H_{3}O^{+}$	17156	64481	62911	58542	14615	9224	10682	$C_{3}H_{9}O^{+} - CH_{4} - H_{2}$	Sequence of dissociation unclear
44.02	13C12CH3O+	601	2159	1999	1936	506	344	317		Isotope ratio varying around 3.3%
26.02	$C_{2}H_{2}^{+}$	43	138	134	167	12	35	33	$C_{3}H_{6}^{+} - CH_{4}$	Dissociation of methane
40.06	$C_3H_4^+$	66	240	192	209	59	46	30	$C_{3}H_{6}^{+} - H_{2}$	Dissociation of hydrogen

Table S13: All detected traces that are peaking with propylene.

The detection of $C_3H_5^+$ first points in towards propyne or allene which form the same ionization products according to [10] but the column used should separate these from propylene. For this reason, we conclude the dissociation of hydrogen to an unusually high degree (around 20% of the $C_3H_7^+$ signal) at our specific conditions, see section E.



Figure S18: *Relative Faradaic Efficiencies of* $C_3H_6 + H_3O^+$ *-related traces.*

Looking at the relative Faradaic Efficiencies of protonated propylene in Fig. S18, it consistently shows an initial stark increase with applied potential, peaking at $U_{\text{Hg/HgO}} = 2.5 \text{ V}$ before dropping off sharply. This behaviour is similar to the one observed for ethylene (see section D.4) where η_{rf} peaks even earlier.

Apart from the ionization products of hydronium, we can also detect species that are clearly ionized by O_2^+ . The initial ion, $C_3H_6^+$ cannot be feasibly separated from the C-13 isotope of $C_3H_5^+$ since the masses are almost identical and the expected intensities of the former are much smaller based on two observations: First, the intensities of the following product, $C_2H_2^+$, are extremely small and second, the isotope ratio of $C_3H_5^+$ is only very slightly above expected levels. This means, that fraction of O_2^+ ionization is smaller than its concentration and therefore has a smaller reaction rate constant than H_3O^+ .

In contrast to ethylene, the trends of Faradaic Efficiencies shown in Fig. S19(b) look the same as the ones in Fig. S18. Even though we see many of the same effects regarding cluster-forming (see S53) and H_3O^+ depletion (see E.2.1), the relative Faradaic Efficiencies appear largely undistorted. The key difference is the fact that we do not see O_2^+ depletion which was probably responsible for the differences discussed in D.4.



S19(a): XIC of $C_3H_6^+$ -related signals at $U_{Hg/HgO} = S19(b)$: Relative Faradaic Efficiencies of $C_3H_6^+$ -2.5V related traces

Figure S19: Analysis of chromatograms and relative Faradaic Efficiencies for C₃H₆⁺- related traces.

A notable irregularity is the $C_2H_5O^+$ trace that we analysed in some detail as a potential candidate to close the mechanistic gap between $C_3H_9O^+$ and $C_2H_3O^+$ via dissociation of methane first and then hydrogen. As can be seen in Fig. S20, there are peaks close to propylene's retention time, but the main signal does not seem to be caused by propylene. They also cannot be ascribed to formalin or acetaldehyde as the former has a much smaller retention time and the latter leads to a distinctive $C_2H_5O^+$ peak shortly after the times shown in the graph.

In section F.3.1, this behaviour was analysed in detail with the help of different reference experiments. The peaks were thereby attributed to two different effects: The first is related to the heating and leads to the perceived peak before propylene's retention time which



Figure S20: Intensity of C₂H₅O⁺ trace over different applied potentials vs. Hg/HgO. A dashed line indicates the location of all other traces peaking with propylene.

can be observed for all GC-PTR-MS experiments. The second is related to the huge signal caused by acetaldehyde eluting shortly after propylene and is only observed for experiments with active eCO2R.

D.7 Acetaldehyde

At this retention time we expect to find acetaldehyde. We expect mostly protonation by H_3O^+ as well as some ionization via residual O_2^+ [9]. Some additional minor secondary and tertiary ions were recorded in a single compound PTR-MS verification experiment.

The ${}^{13}C^{12}CH_3O^+$ trace cannot be separated from the $C_2H_4O^+$ signal since they are both at $m \approx 44.02 \text{ Da}$, which leads to the large isotope ratio, see Tab. S14. According to [9], both O_2^+ products ($C_2H_4O^+$ and $C_2H_3O^+$) should appear in similar concentrations but this is definitely not the case here as the signals detected are an order of magnitude smaller. We only see the ${}^{13}C^{12}CH_3O^+$ increased by a few percent compared to what is expected.

For an overview of the hypothesized PTR reactions, see section E.3.4. For $C_2H_7O^+$ the mechanism is not entirely clear and the isotope ratio is extremely large (consistently between 4% and 5%) which begs the question if either the dissociation of oxygen is not the

D										
Re	tention time	2000	2500	3000	3500	4000	4500	5000		
Peak time in s		626	631	628	630	632	625	623		
Start time in s		609	614	614	610	614	607	606		
Er	nd time in s	654	659	659	655	659	652	651		
			τ.		1					
<i>m/z</i>	Ion assumed		Inte	grated smooth	ied intensity (Normalized co	ounts)		Origin	Comments
45.033	$^{12}C_{2}H_{5}O^{+}$	578655	2120020	1997486	1929370	1899947	2059755	1984097	$CH_3CHO + H_3O^+$	Extremely large signal; Main prod-
										uct of C3H6 protonation with
										H3O+ according to [9]; Detector
	12 12									probably saturated
46.037	¹³ C ¹² CH ₅ O ⁺	12186	53635	83469	91014	99063	78236	47491		Isotope ratio going up from 2.1% to
										more than 5% at medium potentials
										due to saturation
89.058	$C_4H_9O_2^+$	58	277	658	841	935	600	220	$C_2H_5O^+ + CH_3CHO$	Cluster forming
61.029	$C_2H_5O_2^+$								$C_4H_9O_2^+ - C_2H_4$	See discussion below
63.044	$^{12}C_{2}H_{7}O_{2}^{+}$	3169	13306	20709	22406	24264	18402	11124	CH ₃ CHO·H ₃ O ⁺	Second H ₃ O ⁺ product due to large
										concentration (around 1%), not
										documented by [9]
64.047	¹³ C ¹² CH ₇ O ₂ +	94	306	581	616	579	485	281		Isotope ratio varying from 2.0% to
										2.5%
47.013	CH ₃ O ₂ +	220	368	761	721	647	276	1015	$C_2H_7O_2^+ - CH_4$	Dissociation of methane
47.049	$^{12}C_{2}H_{7}O^{+}$	728	2896	3714	4104	4517	3427	2337	$C_2H_7O_2^+ - O_1^+$	Dissociation of oxygen atom?
48.052	13C12CH7O+	-3	132	188	209	202	199	112		Isotope ratio varving between 4%
	, -									and 5%
43.018	$^{12}C_{2}H_{3}O^{+}$	604	1427	2411	2787	2876	2344	1603	$CH_3CHO + O_2^+$	One of two ionization products ac-
	2 9									cording to [9]
44.021	13C12CH3O+	2	84	166	191	143	111	142	$CH_3CHO + O_2^+$	Isotope ratio (up to 10%) indicates
			-							influence of $C_2H_4O^+$ as second
										O_2^+ product [9]
26.016	$C_2H_2^+$	10	134	143	173	167	96	81	$C_2H_4O^+ - H_2O$	Dissociation of water
	- 2 - 2								-2 2 -	

Table S14: All detected traces that are peaking with acetaldehyde.

correct mechanism or if we are observing the influence of ¹⁸O oxygen isotopes and related selectivities.

For the main protonation product $C_2H_5O^+$ we calculate an even larger isotope ratio but in this case is a symptom of detector saturation as described in E.2.3. This is exemplified in Fig. S21(b) where the total fraction of ¹³C signal is increasing and ¹²C is decreasing to the point of maximum acetaldehyde production. Fig. S21(a) shows the actual signal of $C_2H_5O^+$ exhibiting double peaks for most applied potentials.



Figure S21: Illustration of detector saturation experienced for acetaldehyde analysis.

Most likely, the measurement at lowest applied potential $U_{\text{Hg/HgO}} = 2.0 \text{ V}$ yields the actual ¹³C isotope ratio (2.1%) as it does not exhibit the characteristic double peak. For a coherent qualitative analysis of the main protonation product the ¹³C isotope is more suitable in this case though as signals are significantly large for all applied potentials and no detector saturation occurs, see Fig. S22(a). As seen in Fig. S22(b), relative Faradaic Efficiencies are peaking at medium applied potentials which is in line with trends reported in the literature [11]. The key traces ¹³C ¹²CH₅O⁺ and ¹²C₂H₇O₂⁺ show a very coherent trend while ¹²C₂H₇O⁺ and C₄H₉O₂⁺ are in line with expectations of tertiary ions via fragmentation and clustering under conditions of PI depletion discussed in E.2.2.



Figure S22: Analysis of traces related to H₃O⁺ ionization of acetaldehyde.



Figure S23: Analysis of traces related to O_2^+ ionization of acetaldehyde.

As residual O_2^+ does not suffer PI depletion for acetaldehyde (see E.2.1), it is illuminating to study the traces connected to its secondary ions in Fig. S23: The shape of relative FE curve in Fig. S23(b) is very similar of that in Fig. S22(b) but only $C_2H_3O^+$ has a large enough SNR to warrant acceptable uncertainties. The comparatively large value at $U_{Hg/HgO} = 2V$ is probably still caused by noise level for the most part as seen in Fig. S23(a).

A notable irregularity is the $C_2H_5O_2^+$ trace that we analysed in some detail as it shows peaks close to acetaldehyde retention time and could be explained mechanistically by dissociation of ethylene from $C_4H_9O_2^+$ or hydrogen from $C_2H_7O_2^+$. As can be seen in Fig. S24, there are peaks close to acetaldehyde's retention time, but none of them seem to actually caused by acetaldehyde. They also cannot be ascribed to propylene or ethanol as the former has a much smaller retention time and the latter a much larger retention time.



Figure S24: Intensity of $C_2H_5O_2^+$ trace over different applied potentials. A dashed line indicates the location of all other traces peaking with acetaldehyde.

In section F.3.2, this behaviour was analysed in detail with the help of different reference experiments. $C_2H_5O_2^+$ could not be confirmed as an artefact or systematic error as its signal was only detected in experiments with active eCO2R. Moreover, a verification experiment with acetaldehyde as single compound also shows a small signal along with most other traces listed in S14. This lends credibility to the presumed PTR reactions.

D.8 Ethanol

Based on the identified peaks shown in Tab. S15, this is ethanol. Retention times have not been reported for this compound yet, though it fits into the picture with the highest boiling point of the C_2 compounds.

Re	tention time			Applied po	otential vs. F	Ig/HgO in m	V			
		2000	2500	3000	3500	4000	4500	5000		
Peak time in s		717	720	717	718	719	712	710		
St	art time in s	700	703	700	699	701	692	690		
End time in s		750	753	750	749	751	742	740		
m/z	Ion assumed		Integ	grated smoot	hed intensity	(Normalized	Origin	Comments		
47.05	$^{12}C_{2}H_{7}O^{+}$	172549	205754	388661	698355	1204265	1445112	1440198	$C_2H_5OH + H_3O^+$	Main product of ethanol protona- tion with H3O+ according to [13]
48.05	13C12CH7O+	4072	4905	9388	16133	27371	32007	32057		Isotope ratio stable around 2.3%
29.04	$C_{2}H_{5}^{+}$	11543	14333	28598	51301	87134	104305	105251	$C_2H_7O^+ - H_2O$	Dissociation of water
27.02	$C_2H_3^+$	175	200	404	667	1277	1396	1348	$C_2H_5^+ - H_2$	Dissociation of hydrogen
93.07	$C_4H_{13}O_2^+$	128	88	197	409	1184	1601	1732	$C_2H_7O^+ \cdot C_2H_5OH$	Signal very small but somewhat un-
									-2	derestimated since the actual mass
										would be $m = 93.12 \mathrm{Da}$
45.03	$C_2H_5O^+$	3876	5129	8869	11083	13240	12788	10023	$C_2H_7O^+ - H_2$	Hard to separate from descending
										arm of acetaldehyde peak; possibly
										O ₂ ⁺ product
65.06	$^{12}C_{2}H_{9}O_{2}^{+}$	4391	5286	9568	16874	28405	33578	33321	$C_2H_5OH \cdot H_3O^+$	Second H ₃ O ⁺ product due to large
										concentration (around 2%), not
										documented by [13]
66.06	13C12CH9O2+	76	143	197	426	713	825	743		Isotope ratio varies around 2.4%
26.02	$C_{2}H_{2}^{+}$	69	47	36	181	181	255	257	$C_2H_6O^+ - H_2O - H_2$	Possibly dissociations from second
										O2 ⁺ product

Table S15: All detected traces that are peaking with ethanol.

This is the last reported species for which cluster formation due to large concentrations was observed, see section E.3.5. All main traces were verified within the ¹³C experiment.



Figure S25: Analysis of chromatograms and peak areas related to C₂H₅OH.

An interesting case here is the O_2^+ ionization which should be observed as RRC are reported to be similar to H_3O^+ [13]. $C_2H_5O^+$ should be the main product but is first hard to quantify due to overlaps with the much larger acetaldehyde signal as seen in Fig. S25(a) nonetheless its strength is between 1% and 2% of $C_2H_7O^+$ which supports the hypothesis. On the other hand though, no significant signal was detected for $C_2H_6O^+$ which should be the second O_2^+ product - intensities are in an order of magnitude that points towards only ${}^{13}C^{12}CH_5O^+$ though. This might be just another instance where reported product ratios from SIFT are not applicable (see section E.1.1) as $C_2H_2^+$ could be a corresponding product of rapid hydrogen and water dissociation. As we can see in Fig. S25(b), relative Faradaic Efficiency keeps decreasing with applied potential at first but then rises again up to $U_{\text{Hg/HgO}} = 4.0 \text{ V}$ in contrast to the literature where a further decrease in specific current density is reported for larger applied potentials [7]. Most traces' trends agree very well with each other except for $C_2H_2^+$ which can be explained by the small SNR. The curve of the cluster trace's ($C_4H_{13}O_2^+$) relative Faradaic Efficiency significantly below the others is expected behaviour as explained in E.2.2.

D.9 But(adi)ene

Based on reported retention times and observed traces peaking, we expect butene and/or butadiene which is confirmed by secondary ions observed as seen in Fig. S26: Direct protonation products $C_4H_9^+$ and $C_4H_7^+$ as well as traces of $C_3H_6^+$.



Figure S26: Analysis of chromatograms and peak areas related to butene / butadiene.
We analyse the first two traces in some more detail:

- $C_4H_9^+$ is reported for protonation of 2-butene [10] and its signal in Fig. S26(a) shows 3 distinct peaks that indicate the presence of 3 different butene isomers. With increasing potential main signal shifts from second third and then first peak suggesting different selectivities and possibly different reaction paths for butene isomers.
- $C_4H_7^+$ peaks in Fig. S26(b) meanwhile do not coincide with any of the $C_4H_9^+$ and are in fact positioned directly between the first and the second. Butadiene is the most likely origin based on similarity of species and reported retention times.

Fig. S27 shows the different retention times of detected peaks. The small but significant shifts attest to the fact of different species with similar chemical constitution that are just barely separated by the gas chromatography.



Figure S27: Overview of adjusted retention times of but(adi)ene-related traces peaking.

In Fig. S27 we observe 3-4 clusters of peaks throughout all applied potentials. We therefore suggest the following assignments:

- 1. The peak around t = 717 s to 723 s is probably 1-butene. The documented relative retention times agree with 1-butene eluting first.
- 2. The peak around t = 728 s to 733 s is probably butadiene. The C₄H₉⁺ trace is actually at a minimum at this time so it is unlikely to be a butene isomer. Furthermore, documented retention times point towards butadiene as between 1- and 2-butene.
- 3. The latter double peak of $C_4H_9^+$ is probably 2-butene which matches documented retention times and the observation of $C_3H_6^+$ that could indicate a fragment from methyl dissociation [10] but is more likely caused by the artefact discussed in section D.10.
 - (a) Documented retention times suggest peaks at t = 740 s to 747 s to be trans.
 - (b) Documented retention times suggest peaks at t = 757 s to 765 s to be cis.

1-butene peak as described above was separated from the other peaks, peak locations and integrated values are shown in Tab. S16.

Detention time		Appli							
Retention time	2000	2500	3000	3500	4000	4500	5000		
Peak time in s	715	725	721	723	726	717	716		
Start time in s	701	707	709	710	709	699	697		
End time in s	722	729	730	733	738	730	732		
m/z Ion assumed	Inte	egrated si	moothed	intensity	(Norma	nts)	Origin	Comments	
57.07 C ₄ H ₉ ⁺	663	557	934	1632	1883	3683	5487	$C_4H_8 + H_3O^+$	

 Table S16: All detected traces that are peaking with 1-butene.

The distinct 1-butene-related peak of $C_4H_9^+$ was verified by the ¹³C experiment.



Figure S28: Analysis of chromatograms and peak areas related to 1-butene.

In Fig. S28 it is apparent that 1-butene production rises sharply with applied potential and keeps increasing even at $U_{\text{Hg/HgO}} = 5.0 \text{ V}$. It is the first alkene observed that does not exhibit a selectivity peak at smaller applied potentials, compare to D.4 and D.6. The initial high relative Faradaic Efficiency is caused by the large SNR of a small signal combined with small current densities.

Butadiene peak via $C_4H_9^+$ appears separated from the other peaks (via $C_4H_7^+$) - peak locations and integrated values are shown in Tab. S17.

The $C_4H_7^+$ peak is only reliably detectable at small applied potentials, the other values are therefore somewhat skewed and could be declared 0 as done for other species. This is also the reason why it could not be verified by the ¹³C experiment since that operates with a relatively large applied potential.

Data			Appli	ed poten	tial vs. H	lg/HgO i	in mV			
Rete	intion time	2000	2500	3000	3500	4000	4500	5000		
Peak	k time in s	728	731	730	729	733	730	728		
Star	t time in s	719	719 715 715 718 717 722 718							
End	l time in s	745	751	751	745	738	739	732		
m/z	Ion assumed	Inte	egrated si	noothed	intensity	(Norma	Origin	Comments		
55.055	$C_4H_7^+$	370	2021	725	558	120	165	68	$C_4H_6 + H_3O^+$	

Table S17: All detected traces that are peaking with butadiene.



Figure S29: Analysis of chromatograms and peak areas related to butadiene.

In Fig. S29 it is apparent that butadiene production peaks sharply at $U_{\text{Hg/HgO}} = 2.5 \text{ V}$ and is basically non-existent for $U_{\text{Hg/HgO}} > 3.5 \text{ V}$.

2-trans-butene peaks as described above was separated from the other peaks, peak locations and integrated values are shown in Tab. S18.

Retention time Applied potential vs. Hg/HgO in mV										
Keu		2000	2000 2500 3000 3500 4000 4500 5000							
Pea	ık time in s	740	747	744	746	747	741	740		
Sta	rt time in s	725	729	730	733	738	733	735		
Ene	End time in s 756 755 753 756 758 749 745					745				
m/z	Ion assumed	Inte	egrated si	noothed	intensity	(Norma	lized cou	nts)	Origin	Comments
57.07	C ₄ H ₉ ⁺	1973	2144	1342	843	583	400	387	$C_4H_8 + H_3O^+$	
42.04	C ₃ H ₆ ⁺	61	-33	177	42	25	9	11	$C_4H_9^+-CH_3$	appears for few applied potentials only

Table S18: All detected traces that are peaking with 2-trans-butene.

The $C_3H_6^+$ trace is quite low signal-to-noise and only reliably detected for some of the applied potentials. It could also not be verified by the ¹³C experiment so is to be taken



with some caution. Meanwhile, $C_4H_9^+$ was verified with ¹³C as first of a double peak.

Figure S30: Analysis of chromatograms and peak areas related to 2-trans-butene.

The $C_4H_9^+$ peak is very clearly detectable and intensities follow a clear trend of large relative Faradaic Efficiencies at low applied potentials sharply dropping with increased current until at larger applied potentials almost no 2-trans-butene could be detected, see Fig. S30.

2-cis-butene peaks as described above was separated from the other peaks, peak locations and integrated values are shown in Tab. S19.

Rete	ention time	2000	Appli 2500	ed poten 3000	tial vs. H 3500	Ig/HgO i 4000				
Pea	k time in s	765	763	760	762	765	759	757		
Star	rt time in s	756	755	753	756	758	749	745		
End	d time in s	772	780	778	782	780	772	774		
m/z	Ion assumed	Inte	egrated si	moothed	intensity	(Norma	lized cou	nts)	Origin	Comments
57.07	C ₄ H ₉ ⁺	390	3118	2589	1624	744	605	912	$C_4H_8 + H_3O^+$	
42.04	C ₃ H ₆ ⁺	165	5	-47	-13	-32	-32	-33	$C_4H_9^+-CH_3$	appears for few applied potentials only

Table S19:	All c	letected	traces	that	are	peaking	with	2-cis-	butene.
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The $C_3H_6^+$ trace is quite low signal-to-noise and only reliably detected for some of the applied potentials. It could also not be verified by the ¹³C experiment so is to be taken with some caution. Meanwhile, $C_4H_9^+$ was verified with ¹³C as second of a double peak.

The C₄H₉⁺ peak is very clearly detectable and intensities follow a clear trend of sharp increase at low applied potentials (peaking at $U_{\text{Hg/HgO}} = 2.5 \text{ V}$) and then slowly decreasing until at larger applied potentials almost no 2-cis-butene could be detected, see Fig. S31.



Figure S31: Analysis of chromatograms and peak areas related to 2-cis-butene.

D.10 Mass 42 artefact

There are no species expected based on documented retention times at this time. But given the consistent finding of $C_3H_6^+$ as shown in Tab. S20 and the fact that other non-oxygenated C_3 species were detected much earlier, we originally hypothesised this to be cyclopropane.

Table S20: All detected traces that are peaking with mass 42 artefact originally hypothesised as cyclopropane.

Data	ntion time		Appli	ed poten	tial vs. H	lg/HgO i	n mV			
Kett		2000	2500	3000	3500	4000	4500	5000		
Pea	k time in s	778	786	784	787	789	783	777		
Star	Start time in s 773 771 770 772 775 776 764									
Enc	l time in s	794	794 798 795 796 798 796 798							
m/z	Ion assumed	Inte	egrated si	noothed	intensity	(Norma	ized cou	nts)	Origin	Comments
42.042	$C_{3}H_{6}^{+}$	226	589	308	264	342	133	308	$C_{3}H_{6} + O_{2}^{+}$	Reported as main O_2^+ ionization product by [10]

For cyclopropane we would usually expect $C_3H_7^+$ as the main protonation product according to [10] - we do not find peaks at m = 41.04 Da either though. In Fig. S32(b) we see relative Faradaic Efficiencies peaking early at $U_{Hg/HgO} = 2.5$ V but then basically trailing off at a constant level up to larger applied potentials. This behaviour is somewhat similar to the one of 2-butene at earlier retention times and attests to the fact that it is somewhat influenced by it - double peaks for some of the applied potentials indeed had to be separated.

Through the reference experiments described in section F.3.3 the cyclopropane hypotheses was falsified: Within the ¹³C experiment cyclopropane could not be verified as



Figure S32: Analysis of signal and integrated intensities of $C_3H_6^+$ artefact.

the corresponding ${}^{13}C_{3}H_{6}^{+}$ signal does not exhibit a peak, yet ${}^{12}C_{3}H_{6}^{+}$ still does. The same behaviour was seen for reference experiments without eCO2R, confirming this as an artefact with a carbon origin different from CO₂.

D.11 C3H6O isomers

Around t = 850 s to 1000 s a large signal of C₃H₇O⁺ is observed that coincides with documented retention times for acetone. But on closer examination, three distinct peaks can be identified, indicating three constitutional isomers of C₃H₆O that were separated by the column. As shown in Fig. S33, these three species lead to different fragments and ion ratios that can help with identification. These have been verified within the ¹³C experiment.

Based on simple combinatorics, only two C_3H_6O species besides acetone seem realistic: propionaldehyde and allyl alcohol. Most other possible isomers are either less stable tautomers of the afforementioned or ethers. The only non-cyclical ether is methyl vinyl ether and with a significantly differing boiling point and vapour pressure would be expected to elute much earlier than the other compounds. Cyclical compounds seem unlikely: even though a cyclical product has been observed for the first time in this study, its derivatives are even less stable and production is not expected at this rate if at all. Additionally, these three species (acetone, propanal, allyl alcohol) have been observed as eCO2R products before [7].

We assigned the C_3H_6O isomers as following based on retention times, recorded fragments, and observed trends:

1. The peak around t = 862 s to 875 s is most likely propanal as it has the smallest



Figure S33: XICs of traces related to C₃H₆O for different applied potentials.

boiling point of the three and exhibited the largest signal at lower applied potentials as the others which is supported by the literature [7].

- 2. The peak around t = 903 s to 925 s is most likely acetone. Its signal is significantly smaller and peaks barely from the overlapping propanal. This is expected behaviour as its boiling point is only slightly higher and it has been reported as the least-produced of the three isomers [7].
- 3. The peak around t = 985 s to 993 s is most likely allyl alcohol. With a much higher point it elutes significantly later than the first two isomers.

Propanal peak as described above was observed with the highest number of fragments and largest overall signals as shown in Tab. S21.

Within the ¹³C experiment we were able to verify all the main propanal-related traces. A verification experiment with acetaldehyde as single compound showed all ions found to be contributing more than 0.1% of the overall signal above with their expected ratios. The suggested PTR mechanism can be found in section E.3.7. Ratios of all observed isotopes within the original experiment are calculated to be $\approx 3.3\%$. Moreover, even though the signal of ${}^{12}C_{3}H_{7}O^{+}$ is very large, we do not seem to have detector saturation since the isotope ratio does not drop even at peak intensities. These occur at $U_{Hg/HgO} = 2.5$ V before decreasing again with applied potential.

One detected trace peak remains unexplained, at $m/z \approx 64$ Da. This trace was first assigned to the isotope ${}^{13}C{}^{12}CH_7O_2{}^+$ but since ${}^{12}C_2H_7O_2{}^+$ was not detected at all, this suggestion was discarded. It does not seem to be an artefact it can be detected consistently at all applied potentials where the other propanal traces also show large intensities and fol-

R	etention time			Applied pote	ntial vs. Hg/H	HgO in mV				
K	etention time	2000	2500	3000	3500	4000	4500	5000		
Р	Peak time in s	864	870	868	872	874	867	866		
S	Start time in s	835	840	837	839	845	837	837		
E	End time in s	905	910	907	909	915	907	907		
m/z	Ion assumed		Integ	rated smoothed	d intensity (No	ormalized co		Origin	Comments	
59.05	¹² C ₃ H ₇ O ⁺	506760	1546721	1501732	1283260	593135	302796	178824	CH3CH2CHO+H3O+	Large signal; Only propanal proto-
										nation product according to [9]
60.05	13C12C2H7O+	+ 16529	49233	48808	42080	20053	10282	5774		Isotope ratio quite stable at 3.3%
31.02	CH ₃ O ⁺	13971	29425	24311	14739	8645	4747	5215	$C_{3}H_{7}O^{+} - C_{2}H_{4}$	Dissociation of ethylene
41.04	¹² C ₃ H ₅ +	6926	19974	16663	9516	3770	2291	800	$C_3H_7O^+ - H_2O$	Dissociation of water
42.04	13C12C2H5+	353	681	529	300	138	148	21		Signal quite small; Isotope ratio
										varying around 3.3%
39.03	C ₃ H ₃ +	856	688	601	553	425	199	157	$C_{3}H_{5}^{+} - H_{2}$	Dissociation of hydrogen
77.06	12C3H9O2+	2652	8244	6863	4523	2098	1130	564	$CH_3CH_2CHO \cdot H_3O^+$	Second H ₃ O ⁺ product (around
										0.5%), not documented by [9]
78.06	$^{13}C^{12}C_{2}H_{9}O_{2}^{+}$	+ 141	343	235	224	93	59	-18		Small signal-to-noise; Isotope ratio
										varying around 3.3%
61.07	C ₃ H ₉ O ⁺	584	1705	1503	1457	533	396	202	$C_{3}H_{9}O_{2}^{+} - O$	Dissociation of oxygen radical
64.05	unknown	1	177	140	111	75	51	-1		Unknown origin
42.04 39.03 77.06 78.06 61.07 64.05	$\frac{C_{3}H_{3}^{+}}{C_{3}H_{9}O_{2}^{+}}$ $\frac{C_{3}H_{9}O_{2}^{+}}{I^{3}C^{12}C_{2}H_{9}O_{2}^{+}}$ $\frac{C_{3}H_{9}O^{+}}{unknown}$	353 856 2652 + 141 584 1	681 688 8244 343 1705 177	601 6863 235 1503 140	300 553 4523 224 1457 111	138 425 2098 93 533 75	148 199 1130 59 396 51	21 157 564 -18 202 -1	$C_{3}H_{5}^{+} - H_{2}$ $CH_{3}CH_{2}CHO \cdot H_{3}O^{+}$ $C_{3}H_{9}O_{2}^{+} - O$	Signal quite small; Isotope ra varying around 3.3% Dissociation of hydrogen Second H ₃ O ⁺ product (arou 0.5%), not documented by [9] Small signal-to-noise; Isotope ra varying around 3.3% Dissociation of oxygen radical Unknown origin

Table S21: All detected traces that are peaking with propanal.

lows a similar trend. It could not be verified neither within the ¹³C nor the pure compound experiment, which suggests it is some obscure fragmentation like a methylidyne radical $C_3H_9O_2^+ - CH \longrightarrow C_2H_8O_2^+$.



Figure S34: Analysis of chromatograms and peak areas related to propanal.

What is interesting to see is that the peaks of the different traces are not exactly coinciding for some of the applied potentials and in fact seem to shift away from each other with increased applied potential, see Fig. S34(a). We see $C_3H_5^+$, CH_3O^+ , and $C_3H_9O_2^+$ first, then $C_3H_7O^+$ and $C_3H_9O^+$ a few seconds later (up to $\Delta t = 10$ s for $U_{Hg/HgO} > 4.0$ V). These slight shifts illustrated by the red and green dotted lines might be random and seem mostly arbitrary. The main ion ($C_3H_7O^+$) shift towards few seconds later maybe due to overlap of smaller acetone peak and $C_3H_9O^+$ has very flat peak, the exact location is hard to make out. As we can see in Fig. S34(b), relative Faradaic Efficiency peaks early at $U_{Hg/HgO} = 2.5 V$ and decreases with larger applied potentials. Most traces' trends agree very well with each other, the ones with smaller SNR and therefore larger uncertainties deviate somewhat. The ratio of fragments and clusters can be seen to increase for the largest concentrations as expected.

Acetone peak as described above was observed with small signals and massive overlap of propanal's $C_3H_7O^+$ for applied potentials $U_{Hg/HgO} > 2.0V$ as seen in Tab. S22.

Dat	antian tima		Appli	ed potent	tial vs. H	g/HgO i	n mV			
Reti	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	k time in s	-	927	918	925	917	904	908		
Sta	rt time in s	-	893	891	899	895	890	884		
En	d time in s	-	943	941	949	945	940	934		
m/z	Ion assumed	Int	egrated si	noothed	intensity	(Normal	ized cou	nts)	Origin	Comments
59.05	$C_3H_7O^+$	Ca	nnot qua	ntitativel	y disting	uished fro	om propa	nal	CH ₃ COCH ₃ +H ₃ O ⁺	Propanal peak is so broad
			_		-					that it still covers acetone
										peak location
43.06	$^{12}C_{3}H_{7}^{+}$	0	1210	1788	2855	4238	4213	4159	$C_3H_7O^+ - O$	Dissociation of oxygen
44.06	$^{13}C^{12}C_{2}H_{7}^{+}$	0	63	82	43	106	72	231		Isotope ratio varying
										around 2.5%
41.04	$C_3H_5^+$	0	-626	-224	263	647	579	838	$C_3H_7^+ - H_2$	More likely than
										$C_3H_7O^+ - H_2O$

Table S22: All detected traces that are peaking with acetone.

The signals for acetone are very small but sufficient to postulate its existence. The peaks of main traces (or rather main distinguishable traces) were verified within the ¹³C experiment. The prominent $C_3H_5^+$ signal first seems to contradict the postulated acetone as water dissociation via $C_3H_7O^+ - H_2O$ is very unlikely for ketones. Closer analysis reveals an even larger $C_3H_7^+$ signal, indicating subsequent dissociation of atomic oxygen and hydrogen. These traces were reproduced in a verification experiment with pure compound. The signal ratio of $C_3H_7^+$ to $C_3H_5^+$ of 2 to 3 for acetone can be used to unambiguously identify acetone versus propanal with a ratio of ≈ 0.1 .

 $C_3H_7O^+$ should still be dominant. This is almost impossible to verify for most applied potentials due to the massive overlap of the propanal-attributed peak as propanal's concentration seems at least one order of magnitude higher. For larger applied potentials $C_3H_7O^+$ intensities drop to the level of $C_3H_5^+$ though as shown in Fig. S35(a). It is possible that oxygen dissociation is more likely for completely dry acetone. Due to humidity effects, the comparability with reported data or verification experiments is limited when it comes to oxygenated ions.

As shown in Fig. S35(b), acetone exhibits a selectivity trend deviating substantially from the one seen for propanal: although small SNR creates large uncertainties, an increase in relative FE for larger potentials is undeniable with a visible peak at $U_{Hg/HgO} = 4.5$ V.

Allyl alcohol peak as described above can be clearly distinguished from propanal and acetone, all traces are given in Tab. S23.



Figure S35: Analysis of chromatograms and peak areas related to acetone.

Table S23: All detected traces that are peaking with allyl alcohol.

	4: 4:		Ap	plied pote						
Reti	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	ık time in s	991	993	992	990	991	985	984		
Sta	rt time in s	955	964	963	964	968	957	954		
En	d time in s	1015	1024	1023	1024	1028	1017	1014		
m/z	Ion assumed	1	Integrated smoothed intensity (Normalized counts)						Origin	Comments
59.05	C ₃ H ₇ O ⁺	2495	1874	2790	4297	5751	6239	6383	$CH_2CHCH_2OH + H_3O^+$	
41.04	$^{12}C_{3}H_{5}^{+}$	5026	6635	10644	18128	27787	32257	29084	$C_3H_7O^+ - H_2O$	Distinguishable peak
										before larger peak
42.04	$^{13}C^{12}C_{2}H_{5}^{+}$	142	228	439	601	959	948	1053		Isotope ratio oscillat-
										ing around 3%
39.03	$C_{3}H_{3}^{+}$	265	247	586	641	605	896	1094	$C_{3}H_{5}^{+} - H_{2}$	Distinguishable peak
										before larger peak

Main traces were verified within ¹³C experiment. Even though $C_3H_5^+$ and $C_3H_3^+$ peaks at this time are shortly followed by larger peaks as shown in Fig. S36(b) (mostly pentene), we were able to separate contributions.

The relative Faradaic Efficiencies shown in Fig. S36(c) show a similar trend but the different curves are not very coherent. This is caused by the very small signals amongst large noise levels for small applied potentials as seen in Fig. S36(a) and the amplification of these when dividing by the small current densities. This is a common occurence and corrected in our workflow by neglecting the values and traces with too large SNR. To illustrate this, Fig. S36(d) shows corrected relative FE for all traces with sufficient SNR. The values for $U_{Hg/HgO} = 2.0$ V have been neglected in accordance with the red highlights in Tab. S23. This shows the $C_3H_5^+$ trace to be in good agreement with the others and therefore representative for allyl alcohol. It shows an initial peak of Faradaic Efficiencies for small applied potentials that first decrease and then increase again with larger poten-



Figure S36: Analysis of chromatograms and peak areas related to allyl alcohol.

tials. It peaks again around 4.0 V to 4.5 V with only slightly larger selectivities than for 2.0 V.

D.12 Pentene and propanol

Around t = 1000 s to 1100 s we observe peaks of a few C₃ traces. The large C₃H₇⁺ signal in combination with the smaller C₃H₉O⁺ signal as well as its boiling point close to allyl alcohol strongly suggest propanol as the source. Seemingly contradictory, we also find C₅H₁₁⁺, which hints towards pentene production.

Upon analysis of precise peak times as shown in Fig. S37, a slight difference between C₃



Figure S37: Chromatograms of traces peaking around $t \approx 1020$ s for different applied potentials.

and C_5 is apparent for larger applied potentials. This is indicated by the two dashed lines in Fig. S37(b). On closer examination, the $C_3H_3^+$ trace is showing a peak at both times. We therefore hypothesize pentene as well as propanol production which was just barely separated by GC column.

Pentene was observed for t = 1011 s to 1029 s which coincides quite well with its expected relative retention time. Detected signals are listed in Tab. S24. While the C₃H₃⁺ trace can be unambiguously identified as peaking with pentene as well as propanol for most applied potentials, the overlap is so substantial and overall SNR so low that the separated signal is hardly quantifiable. For this reason, its values are highlighted yellow.

Dat	antion time		App	lied pote	ntial vs. H	Ig/HgO i	in mV			
Reu	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	ık time in s	-	1027 1026 1019 1013							
Sta	rt time in s	-	-	-	1002	1003	998	992		
En	d time in s	-	-	-	1082	1083	1078	1072		
m/z	Ion assumed	In	tegrated	smoothe	d intensity	(Norma	lized cour	nts)	Origin	Comments
71.09	C ₅ H ₁₁ +	-	-	-	103	486	555	1022	$C_5H_{10} + H_3O^+$	Only documented proto- nation product of pentene [14]
39.03	C ₃ H ₃ ⁺	-	-	-	3376	2853	2585	$C_{3}H_{5}^{+}-H_{2}$	Other origins possible, multiple subsequent disso- ciations necessary	
41.04	C ₃ H ₅ +) C	annot qu	antitative	ely disting	uished fr	om propa	nol	$C_{3}H_{7}^{+}-H_{2}$	Possibly other origin
43.06	C ₃ H ₇ ⁺	Cannot quantitatively distinguished from propanol						nol	$C_5H_{11}^+ - C_2H_4$	Ethylene dissociation

Table S24: All detected traces that are peaking with pentene.

The question remains, which pentene isomer we found. We argue that at least the main

portion of it will be 1-pentene for a few reasons. First of all, retention time and PTR products coincide with what is documented in the literature for 1-pentene. But since other isomers are not as well-documented, they might possibly look very similar. Here we can use analogy to the well-observed butene peaks from D.9 as second reason: the relative Faradaic Efficiency increasing with applied potential shown in Fig. S38(b) resemble the trends observed for 1-butene and corresponds well to the mechanism proposed for alk-1-enes in the main text.



Figure S38: Analysis of chromatograms and peak areas related to pentene.

When looking at $C_5H_{11}^+$ trace closely in Fig. S38(a), we see a slightly stretched peak or even a second peak around 10s to 30s after the main peak which hints towards a very small fraction of 2-butene also being produced. This is more pronounced for the slightly smaller applied potentials which lends additional credibility to this theory in analogy to butene and the proposed mechanism for alk-2-enes. A possible third peak can even be seen ≈ 50 s later, which again hints at the existence of both stereoisomers in analogy to butene.

The large majority of the small amount of pentene produced will still be 1-pentene as 1butene also dominated the butene production (partially due to larger total current densities at applied potentials where the alk-1-enes exhibit their largest Faradaic Efficiency). The $C_5H_{11}^+$ peak was verified within the ¹³C experiment. It even shows the triple peak indicating afforementioned isomers as the current is comparable to the one at $U_{Hg/HgO} = 4.5$ V in the main experiment.

Propanol was observed for 1027 s to 1048 s with a number of traces listed in Tab. S25. All key species detected were verified by the C13 experiment, our hypothesized PTR mechanism is shown in section S56.

D				Applied pot	ential vs. Hg	g/HgO in m	V		1	
Rei	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	ak time in s	1041	1042	1030	1029	1030	1023	1024		
Sta	rt time in s	1007	1006	1002	1001	1002	1001	1002		
Er	d time in s	1102	1101	1097	1096	1097	1096	1097		
m/z	Ion assumed		Integr	ated smooth	ed intensity (Normalized	counts)		Origin	Comments
61.07	C ₃ H ₉ O ⁺	262	501	1403	2093	2311	2003	1698	C ₃ H ₇ OH+H ₃ O ⁺	Initial protonation product but ac- cording to [13] only 10%-20%
43.06	$^{12}C_{3}H_{7}^{+}$	80428	180829	478402	723575	840705	687309	608056	$C_3H_9O^+-H_2O$	Main protonation product accord- ing to [13]
44.06	13C12C2H7+	2727	5714	14735	22028	26232	21358	18789		Isotope ratio very stable at 3.1%
41.04	12C3H5+	10904	25896	74688	111755	125898	103751	91558	$C_{3}H_{7}^{+} - H_{2}$	First hydrogen dissociation
42.04	13C12C2H5+	476	873	2412	3498	3599	2959	2678		Isotope ratio varying around 3.1%
39.03	$C_3H_3^+$	618	-307	1902	3468	3000	2650	2495	$C_{3}H_{5}^{+} - H_{2}$	Second hydrogen dissociation
27.02	$C_2H_3^+$	341	603	1601	2359	2757	2231	1992	$C_{3}H_{7}^{+} - CH_{4}$	Dissociation of methane
79.05	$C_3H_{11}O_2^+$	-16	114	210	256	257	186	270	C ₃ H ₇ OH·H ₃ O ⁺	Signal underestimated since the actual mass would be $m = 79.08 \text{ Da}$

Table S25: All detected traces that are peaking with propanol.

In this case, identifying the specific isomer is difficult. According to SIFT literature [13], 1-propanol (or n-propanol) and 2-propanol (or i-propanol) lead to slightly different product distributions in $C_3H_7^+$ and $C_3H_{90}^+$ (90:10 vs. 80:20). Since we observe almost exclusively $C_3H_7^+$ (more than 99%), this might hint towards 1-propanol or just the fact that in our specific PTR conditions, water dissociation after protonation is dominant. We do not observe any of the O_2^+ ionization products either which is notable given the large intensities for some of the H_3O^+ products and similar rate coefficients according to [13].

As Baasandorj et al. [15] observed a very similar fragmentation pattern (and also the dominance of $C_3H_7^+$ versus $C_3H_{90}^+$) for small humidities and comparable reduced field strength, we decided to carry out additional verification experiments using the pure compounds 1-propanol and 2-propanol. The resulting signal ratios are shown in Tab. S26.

Table S26: Signal ratios detected using internal standards of pure compound compared to the average signal ratios detected at this retention time.

ion signal ratio	1-Propanol	2-Propanol	eCO2R GC-MS
$C_3H_7^+$ / total	57.83%	74.23 %	85.03 %
$C_3H_5^+$ / total	38.40%	23.42 %	14.07 %
$C_3H_3^+$ / total	2.03%	1.01 %	0.35 %
$C_2H_3^+$ / total	1.45%	0.31 %	0.27 %
$C_3H_9O^+$ / total	0.26%	0.82 %	0.24 %
$C_{3}H_{11}O_{2}^{+}$ / total	0.02%	0.21 %	0.03 %
C ₃ H ₅ ⁺ / C ₃ H ₇ ⁺	66.40%	31.55%	16.55%
$C_{3}H_{3}^{+}/C_{3}H_{5}^{+}$	5.29%	4.31%	2.49%
$C_{3}H_{11}O_{2}^{+}/C_{3}H_{9}O^{+}$	7.69%	25.61 %	12.50 %

These experiments seem to suggest the presence of 2-propanol rather than 1-propanol as most signal ratios are closer to the reference. This is not definitively conclusive as there are arguments for both: 1-Propanol is the obvious candidate as it is the only isomer so far reported to be produced from CO2R [7]. Its boiling point coincides with that of allyl alcohol and therefore makes sense to elute at almost the same time (see section D.11). While the signal ratios of unoxygenated ions does not coincide with the pure compound

this might be caused by overlap with pentene - meanwhile, the signal ratios of oxygenated species are closer to the reference of 1-propanol. On the other hand, substantial pentene overlap does not seem very likely considering its C_5 signal as well as the agreement of selectivity trends for oxygenated and unoxygenated species alike (see Fig. S39(b)). Furthermore, $C_3H_{11}O_2^+$ signal is underreported so the actual ratio might be also closer to 2-propanol as all the others are.

The main issue with verification is that the eCO2R-GC-MS system cannot be adequately replicated as there are always cross-interactions of species as well as effects of the gas chromatography - most notably the lack of humidity in the drift chamber at most times. We might have a mixture that is not separated. The peaks are quite flat and stretched, some minor fragments like $C_3H_3^+$ and $C_2H_3^+$ even indicate a double peak.

Another indicator for 2-propanol is the slight but consistent shift in signal fractions with increasing applied potentials as depicted in Fig. S39(a). A relative decrease of $C_3H_7^+$ while $C_3H_5^+$ signal fraction is increasing indicates different potential dependent behaviour of 1- and 2-propanol. Still, the evidence is not sufficient to make any definitive claims.



Figure S39: Analysis of signal fractions and peak areas related to propanol.

While substantial propanol production is observed for all applied potentials, Faradaic Efficiency peaks around $U_{Hg/HgO} = 3.5 \text{ V}$ as shown in Fig. S39(b).

D.13 Butanedione

Around t = 1225 s to 1234 s a double-oxygenated C₄ species is observed. The signals are listed in Tab. S27 and attributed to butanedione. Based on boiling temperatures, one might expect it to elute shortly after butanone instead of the observed ≈ 30 s prior to it, but boiling points are only a rough indicator.

Applied potential vs. Hg/HgO in mV Retention time 2000 2500 3000 4000 4500 5000										
-		2000	2300	5000	5500	4000	4500	5000		
Pe	ak time in s	1228	1232	1231	1232	1234	1227	1229		
Sta	art time in s	1180	1185	1182	1185	1193	1184	1184		
Er	nd time in s	1270	1275	1272	1275	1283	1274	1274		
m/z	Ion assumed		Integ	grated smoot	hed intensity	(Normalize	d counts)		Origin	Comments
87.05	$C_4H_7O_2^+$	237	4018	15217	26670	43015	24220	11523	$C_4H_6O_2 + H_3O^+$	Main protonation product expected butanedione [16]
43.02	$^{12}C_2H_3O^+$	3612	68290	316036	571020	903242	505910	244256	$\mathrm{C_4H_7O_2^+}-\mathrm{CH_3CHO}$	Main O ₂ ⁺ ionization product ex- pected especially for butanedione [16] but signal very large
44.02	13C12CH3O+	187	1492	6830	12137	19359	10716	5481		Isotope ratio stable around 2.2%

Table S27: All detected traces that are peaking with butanedione.

These traces as well as their ratios shown in Fig. S40(a) have been verified within the ¹³C experiment. As there are quite a number of possible $C_4H_6O_2$ structural isomers, detailed analysis is necessary for clear identification. Unfortunately, only ionization data available os for 2,3-butanedione [16]. Even though the $C_2H_3O^+$ fragment was not reported in that SIFT study [16], we can safely assume it comes from easy acetaldehyde dissociation after H_3O^+ ionization under given conditions. Due to the large protonation signal and missing $C_4H_6O_2^+$ peak we can exclude the possibility of O_2^+ ionization pathway.



Figure S40: Analysis of chromatograms and peak areas related to butanedione.

We can infer expected ionization products for 1,4-butanedial based on available data on other aldehydes though [17]: easier dissociation of H_2O would definitely expected, therefore $C_4H_5O^+$ signal; as well as breaking into more and different fragments. The same applies to some extent for a mixed molecule with a single aldehyde group (keto-butanal). Moreover, the boiling temperatures of these two structural isomers would be considerably higher which makes elution at this time less likely.

Since diols would require a triple bond or two double bonds which is mechanistically unlikely, they can be safely neglected to be produced at this considerable rate. The only remaining group to consider are esters. Based on the fragmentation patterns expected for an ester [18], only vinyl acetate comes into question which also exhibits a boiling point slightly smaller than butanone. Considering the single ester that we unambiguously identify in this study (ethyl acetate, see section D.15) though, we would expect overall less fragmentation and a wider range of fragments (e.g., double-oxygenated C_2 fragment). For this reason, the detected signals summarized in Fig. S40 are identified as 2,3-butanedione (diacetyl).

In Fig. S40 the relative Faradaic Efficiencies calculated for the traces related to butanedione are lining up very neatly in this case which indicates that there are no isomers with a slightly different mechanism or product distribution. Faradaic Efficiency for butanedione is seen to exhibit a sharp peak at $U_{Hg/HgO} = 4.0$ V.

D.14 C4H8O isomers

Around t = 1310 s to 1320 s a large signal of C₄H₉O⁺ suggests the existence of C₄H₈O species. A second trace of C₄H₇⁺ is also recorded, see Tab. S28.

	Applied potential vs. Hg/HgO in mV									
Ret	ention time	2000 2500 3000 3500 4000 4500 5000								
Pea	ık time in s	1311	1318	1316	1320	1321	1314	1312		
Sta	rt time in s	1245	1250	1259	1262	1258	1256	1252		
En	d time in s	1365	1370	1379	1382	1378	1376	1372		
m/z	Ion assumed		Integrated	l smoothed	d intensity	(Normali	zed counts	5)	Origin	Comments
73.07	C ₄ H ₉ O ⁺	8633	31150	59063	92019	75827	47803	25554	$C_4H_8O^+ + H_3O^+$	Main protonation product of n-butanal according to [17]
55.06	C ₄ H ₇ +	791	4162	4221	2490	1578	777	590	$\mathrm{C_4H_9O^+-H_2O}$	Dissociation of water; mi- nor protonation product of n-butanal according to [17]

Table S28: All detected traces that are peaking with butanal/butanone.

When comparing the two traces, it becomes apparent that there is a time shift of ≈ 15 s between the two: while $C_4H_9O^+$ is the dominant trace with a bell-shaped peak at a distinct time, $C_4H_7^+$ exhibits a flatter shape with either a single peak a few seconds earlier or a double peak where the second one coincides with $C_4H_9O^+$. This is illustrated in Fig. S41(a) through Fig. S41(c) where peak locations of the two traces are indicated by dashed lines. The signal fractions shown in Fig. S41(d) are not stable and seen to decrease substantially over time which suggests that more than one C_4H_8O molecule is present. The two traces as well as the time shift has been verified within the ¹³C experiment.



Figure S41: Analysis of signals related to C₄H₈O across different applied potentials.

In order to identify the different C_4H_8O species, the anaology to identified C_3H_6O isomers can be used. These C_3H_6O molecules are listed in Tab. S29 with PTR product and fragment ratios as well as other transferable information. Based on this, we can discuss the three possible analogous C_4 species: Butanal, butanone and butenol (crotyl alcohol). Unfortunately, none of the (more discriminating) O_2^+ products were found.

Since we see a similar shift between $C_3H_7O^+$ to $C_3H_5^+$ in D.11, indicating the barely separated propanal and acetone, it can be speculated that the shifted $C_4H_9O^+$ and $C_4H_7^+$ peak indicate barely separated butanal and butanone. This is supported by similar differences in boiling points for the C_4H_8O species, which leads us to expect butanone to elute shortly after butanal. Crotyl alcohol would be expected to elute significantly later and is apparently not observed.

Molecule	Time	$C_{3}H_{7}O^{+}$ / $C_{3}H_{5}^{+}$	$ U_{\mathrm{Hg/HgO}}(\eta_{rf}=1)$
propanal	$\begin{vmatrix} \approx 870 s \\ \approx 920 s \\ \approx 990 s \end{vmatrix}$	$\approx 1\%$	2.5 V
acetone		$\approx 5\%$	4.0 V
allyl alcohol		$\approx 500\%$	4.5 V

Table S29: *Comparison of identified* C₃H₆O *species for* C₄H₈O *assignment.*

One remaining issue is the fact that we would not ascribe any $C_4H_7^+$ to butanone while acetone even has a larger $C_3H_5^+$ to $C_3H_7O^+$ ratio than propanal. But as explained in D.11, this fragment is in acetone's case not created by water dissociation but rather subsequent dissociation of atomic oxygen and hydrogen. Measuring butanone standard solution with the PTR-MS, we were able to confirm no $C_4H_7^+$ and almost pure $C_4H_9O^+$ as result of its protonation.

As the two species are overlapping this much, signals cannot be separated in a meaningful way. For this reason, we assign the $C_4H_7^+$ signal completely to butanal and $C_4H_9O^+$ completely to butanone as we are not interested in absolute concentration but only relative trends. The butanal selectivity trend will be completely accurate but the butanone trend will be skewed towards butanal.



Figure S42: Relative Faradaic Efficiency of traces representing n-butanal and butanone.

Butanal is represented by the $C_4H_7^+$ trace for further analysis which has been reported as minor protonation product also in SIFT studies [9] [17]. Two isomers are technically possible: n-butanal (butyraldehyde) and i-butanal (2-methyl-propanal). According to [17], only n-butanal leads to a small fraction of $C_4H_7^+$. As the signal fraction for smaller applied potentials (where we expect aldehyde production to dominate over ketone production, see main text) is close to the expected 5% we suggest n-butanal as the only C_4H_8O isomer produced as i-butanal would also be mechanistically unlikely.

Fig. S42 shows butanal's Faradaic Efficiency (represented by $C_4H_7^+$ trace) peaking at relatively small applied potential, declining rapidly at increasing potentials. This trend is very similar to propanal which reaches its peak Faradaic Efficiency at the same applied potential.

Butanone protonation is not well-documented but our verification experiment confirmed the dominance of $C_4H_9O^+$ and complete absence of $C_4H_7^+$. Its relative Faradaic Efficiency represented by the $C_4H_9O^+$ trace shown in Fig. S42 indicates peak selectivities shifted towards slightly larger potentials than butanal. A similar trend is seen for acetone and propanal but is more pronounced with Faradaic Efficiency peaking for even larger potentials. This can be explained by the partial attribution of $C_4H_9O^+$ trace to butanal, skewing the results a bit.

D.15 Ethyl Acetate

Even though, according to documented relative retention times it would be expected a few minutes earlier, the traces found with a distinct peak at At t = 1319s to 1414s all point towards ethyl acetate.

Applied potential vs. Hg/HgO in mV										
Rete	ention time	2000	2500	3000	3500	4000	4500	5000		
Peal	k time in s	1397	1398	1396	1398	1403	1392	1395	1	
Star	t time in s	1332	1331	1338	1331	1332	1329	1327		
End	l time in s	1462	1461	1468	1461	1462	1459	1457		
m/z	Ion assumed		Integrat	ed smoothe	ed intensity	(Normalize	ed counts)		Origin	Comments
89.06	C ₄ H ₉ O ₂ ⁺	880	3873	11316	24635	30367	18980	10285	CH ₃ COOC ₂ H ₅ +H ₃ O ⁺	Only SIFT product according to
										[18]
61.03	$C_2H_5O_2^+$	2584	4603	16715	37464	46884	29969	18705	$C_4H_9O_2^+ - C_2H_4$	Most prominent PTR fragment ac-
										cording to [15]
43.02	$C_2H_3O^+$	474	1155	3196	5824	7170	5657	2028	$C_2H_5O_2^+ - H_2O$	Second fragment according to [15]
107.07	$C_4H_{11}O_3^+$	Sign	al-to-nois	e ratio so la	ow, that it co	annot be pr	operly qua	ıtified	CH ₃ COOC ₂ H ₅ ·H ₃ O ⁺	
91.08	C ₄ H ₁₁ O ₂ +	166	165	181	501	1242	1267	777	$C_4H_{11}O_3^+ - O$	Dissociation of oxygen radical
79.04	C2H7O3+	56	-8	79	206	468	423	253	$C_4H_{11}O_3^+ - C_2H_4$	ethylene dissociation

Table S30: All detected traces that are peaking with ethyl acetate.

Signals recorded correspond very well with masses documented by Baasandorj et al. [15]: the main traces of protonated ethyl acetate $(C_4H_9O_2^+)$, fragments after subsequent dissociation of ethylene $(C_2H_5O_2^+)$ and water $(C_2H_3O^+)$, as well as the equivalents of the first two clustered with one water molecule $(C_4H_{11}O_3^+ \text{ and } C_2H_7O_3^+)$ are documented. The first three main traces were also verified with the ¹³C experiment, see section F.4.6. We interpret the ones with additional water to stem from clustering with hydronium rather than residual humidity due to the GC separation though, see section E.3.8. This does not make a difference effectively as trace intensities also fit quantitatively: around 35% $C_4H_9O_2^+$, 50% $C_2H_5O_2^+$ and 15% $C_2H_3O^+$ correspond well with what was measured for $E/N \approx 114$ Td at lowest relative humidity.

The ions clustered with water show relatively small signal-to-noise ratio which is why they are not really suitable for quantitative statements, see Fig. S43(a). One of the traces

found, $C_4H_{11}O_2^+$, is indeed not documented in the literature - even though it shows higher intensities for some of the applied potentials than $C_4H_{11}O_3^+$, which we assume to be the precursor. The dissociation of an oxygen radical that has been hypothesized for multiple PTR reaction mechanisms in this work, seems to be quite fast.



Figure S43: Analysis of chromatograms and peak areas related to ethyl acetate.

As the recorded signals fit the literature for ethyl acetate very well, identification is unambiguous. For any other type $C_4H_8O_2$ isomer, different traces would be expected (for example water dissociation for aldehydes). The other possible ester, methyl propionate, can also be safely discarded as no $C_3H_5O^+$ is observed [18]. For the first time, an ester has been identified as eCO2R product as formation via a subsequent bulk reaction also seems unlikely. Fischer esterification is quite slow, requires adetic acid and is accelerated by acid catalysis which is contradicted by our large pH. Tishchenko reaction of two acetaldehydes might seem possible due to alkaline milieu and large acetaldehyde signal, but selectivity trends are clearly different as seen in Fig. S43(b): While Faradaic Efficiency of acetaldehyde peaks at $U_{Hg/HgO} = 3.0V$, ethyl acetate shows largest FE at $U_{Hg/HgO} = 4.0V$. The same applies to ethanol hydrogenation: this route is technically possible and could even be catalysed by copper, but the contrast of potential dependence (see rFE over current) between supposed reactant and product refute this. Finally, most of the mentioned bulk reactions are quite slow and would not affect rates considerably within the mild conditions and small time scales considered in this study.

D.16 Pentanedione

Around t = 2100 s to 2500 s we observe peaks of a traces that strongly suggest C₅H₈O₂ as the source. The key trace, C₅H₉O₂⁺, is accompanied by a fragment, C₂H₃O⁺ for both of the two distinct peaks observed. Analogous to D.13, this points towards pentanedione

or pentanedial. As we can see in Fig. S44, the first peak is much smaller and somewhat overlapped by the larger peak following it.



Figure S44: *XICs of traces peaking around t* \approx 2100s *to* 2500s *for different applied potentials.*

Both of these traces as well as their rough intensity ratios were verified within the ¹³C experiment. Regarding the species identification, we can argue analogous to butanedione in D.13. Again, esters are unlikely as no double-oxygenated fragments can be found. The two esters in question would be allyl acetate and isopropenyl acetate but their boiling points are so similar that they might not be separated at all.

The documented protonation products of pentanedial include $30\% C_5H_7O^+$ [9] which we do not observe here. We do observe the fragment possibly caused by acetaldehyde dissociation though, $C_2H_3O^+$, albeit at a much larger fraction than the suggested 20%. While different fractions were observed for many of the C_{3+} hydrocabons and might be caused by increased electric fields, we would nonetheless expect to observe at least some water dissociation (and therefore $C_5H_7O^+$) for aldehydes and especially dialdehydes.

As mentioned, we do observe a large amount of $C_2H_3O^+$, which is reported as third H_3O^+ ionization product for dial [9]. For the dione it is only reported as an O_2^+ ionization product [16], but similar to the butanedione discussion (see section D.13) we probably see this fragmentation also via H_3O^+ with our specific PTR setup and parameters. Based on molecule geometry we would expect this fragmentation to occur twice as often for 2,4-pentanedione than for 2,3-pentanedione (which is equally likely to produce $C_3H_5O^+$).

In fact, we do see a significant difference in intensities of the fragment relative to the protonated pentanedione. We therefore ascribe the two peaks to pentanedione isomers:

1. The peak around $t \approx 2200$ s is propably 2,3-pentanedione as fragment (by propanal dissociation on one side) signal is approximately ten times larger than protonated

pentanedione signal. Fragmentation could technically also produce $C_3H_5O^+$ fragment (by acetaldehyde dissociation on the other side), but could not be verified.

2. The second peak around $t \approx 2350$ s is probably 2,4-pentanedione as fragment (by acetone dissociation on either side) signal is approximately twenty times larger than protonated pentanedione signal.

This is supported by the elution sequence matching expectations based on boiling points.

2,3-pentanedione is detected at t = 2196 s to 2222 s, signals are listed in Tab. S31.

Dat	Retention time Applied potential vs. Hg/HgO in mV									
Reb	ention time	2000 2500 3000 3500 4000 4500 5000								
Pea	ık time in s	2219	2218	2213	2218	2205	-	-		
Sta	rt time in s	2150	2139	2128	2142	2145	-	-		
En	d time in s	2270	2259	2248	2262	2265	-	-		
m/z	Ion assumed		Integrated	smoothed	l intensity	(Normaliz	ed counts)	Origin	Comments
101.06	$C_5 \mathrm{H_9O_2}^+$	504	1222	358	346	328	0	0	$C_{5}H_{8}O_{2}+H_{3}O^{+}$	Main protonation product accord- ing to [16]
43.02	$^{12}C_{2}H_{3}O^{+}$	3053	7580	4495	2594	2057	0	0	$C_5H_9O_2^+ - C_2H_5CHO$	Consistently around 85% - 90% of the signal
44.02	¹³ C ¹² CH ₃ O ⁺	Signal-	to-noise r	atio so lov	v, that it co	annot be p	roperly qu	antified		Where detected, isotope ratio around 2.5%

Table S31: All detected traces that are peaking with 2,3-pentanedione.

As shown in Fig. S45, Faradaic Efficiency of 2,3-pentanedione production seems to be highest for small applied potentials ($U_{\text{Hg/HgO}} = 2.5 \text{ V}$ specifically) and is decreasing sharply with larger potentials.



Figure S45: Analysis of chromatograms and peak areas related to 2,3-pentanedione.

	Table S32	2: All	detected	traces	that	are	peaking	with 1	2,4-	pente	aned	ione	2
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Applied potential vs. Hg/HgO in mV										
Keit	ention time	2000	2500	3000	3500	4000	4500	5000		
Pea	k time in s	2338	2345	2344	2343	2345	2339	2339		
Star	rt time in s	2268	2269	2262	2261	2268	2270	2271		
Enc	d time in s	2448	2449	2442	2441	2448	2450	2451		
m/z	Ion assumed		Integrate	ed smoothed	d intensity (Normalize	d counts)		Origin	Comments
101.06	C5H9O2+	304	3585	5584	4490	1507	952	606	$C_5H_8O_2 + H_3O^+$	Direct protonation product
43.02	$^{12}C_{2}H_{3}O^{+}$	9866	60060	90550	81659	28225	12789	7376	$C_5H_9O_2^+ - C_2H_5CHO$	Consistently around 95% of the sig-
										nal
44.02	¹³ C ¹² CH ₃ O ⁺	-107	1248	2186	1673	424	546	46		Isotope ratio around 2.2%

2,4-pentanedione is detected at t = 2320 s to 2389 s, signals are listed in Tab. S32.

As shown in Fig. S46, the selectivity trend for 2,4-pentanedione deviates from that of its isomer. Its Faradaic Efficiency peaks for medium applied potentials ($U_{\text{Hg/HgO}} = 3.0$ V specifically) and is decreasing again with larger potentials.



Figure S46: Analysis of chromatograms and peak areas related to 2,4-pentanedione.

D.17 Overview of detected species

All detected carbon-containing species are listed with properties of interest in Tab. S33.

Table S33: Overview of all detected carbon-containing species. Information on species makeup is given as reduction state R, number of carbon and oxygen atoms, C and O. The observed retention time t_{ret} is given alongside an indicator of certainty for this product. For the calculated relative FE the selected representative trace is given with a measure for the applied potential vs. RHE at which the FE is expected at a maximum, U_{RHE}^{max} .

anaoiaa	n	nakeu	р	identificat	ion	(relative) Fai	adaic Efficiency η_{rf}	commont
species	R	С	0	confirmed?	$t_{\rm ret}$ [s]	trace	$U_{\rm RHE}^{\rm max} [{ m mV}]$	comment
carbon dioxide	0	1	2	educt	232	$\rm CO_2H^+$		
carbonic acid	0	1	3	educt	230	$H_2CO_3H^+$		
carbon monoxide	2	1	1	known	134	$CO \cdot H_3O^+$	> -700	
formaldehyde	4	1	1	known	431	CH ₃ O ⁺	> -700	
methanol	6	1	1	known	426	CH_5O^+	> -700	
methane	8	1	0	known	174	CH ₅ O ⁺	≤ -1500	O_2^+ product used
acetaldehyde	10	2	1	known	630	$C_2H_7O_2^+$	-1000 to -900	partial PI depletion
ethylene	12	2	0	known	339	$C_2H_5^+$	-1000 to -800	partial PI depletion
ethanol	12	2	1	known	718	$C_2H_7O^+$	-1500 to -1300	
propanal	16	3	1	known	872	$C_3H_9O_2^+$	-850 to -750	traces shown to reduce
acetone	16	3	1	known	925	$C_3H_7^+$	≈ -1300	races chosen to reduce
allyl alcohol	16	3	1	known	990	$C_{3}H_{5}^{+}$	-1500 to -1300	
propylene	18	3	0	known	550	$C_3H_4^+$	≈ -750	O_2^+ product used
1-propanol	18	3	1	known	1029	$C_{3}H_{7}^{+}$	_1200 to _ 1100	not separable
2-propanol	18	3	1	unconfirmed	1029	$C_3H_7^+$	-1200 10 - 1100	not separable
butanedione	18	4	2	verified	1232	$C_2H_3O^+$	≈ -1300	verified by C ₄ H ₇ O ₂ ⁺
ethyl acetate	20	4	2	verified	1398	$C_4H_9O_2^+$	-1300 to -1100	
butadiene	22	4	0	confirmed	729	$C_4H_7^+$	-850 to -750	
butanal	22	4	1	confirmed	1320	$C_4H_7^+$	-850 to -750	
butanone	22	4	1	confirmed?	1310	$C_4H_9O^+$	-1200 to -1100	influenced by butanal
1-butene	24	4	0	verified	723	$C_4H_9^+$	< -1500	
2-cis-butene	24	4	0	verified	762	$C_4H_9^+$	-850 to -750	
2-trans-butene	24	4	0	verified	746	$C_4H_9^+$	> -700	
2,3-pentanedione	24	5	2	verified	2218	$C_2H_3O^+$	-850 to -750	verified by $C_{a}H_{a}O_{a}^{+}$
2,4-pentanedione	24	5	2	confirmed	2343	$C_2H_3O^+$	-1000 to -800	vernied by C511902
1-pentene	30	5	0	verified	1027	$C_5H_{11}^+$	< -1500	not separable
2-pentene	30	5	0	unconfirmed	1023	$C_5H_{11}^+$	signal too small	

Observed retention times in this table are given in seconds rather than minutes to better distinguish species eluting only seconds apart from each other. For the sake of simplicity, only a single time is mentioned (observed for the experiment with $U_{Hg/HgO} = 3.5 \text{ V}$) as the small variations between experiments are self-consistent and thus not meaningful for this analysis.

In order to discuss the mechanistic implications of the described experiments, it is important to keep in mind the reduction state R of each species. This measure gives the number of reduction steps (i.e. electrons transferred) necessary to produce this compound from one or multiple carbon dioxide molecules. Based on observed trends in relative Faradaic Efficiencies and Kinetic Isotope Effect, hypotheses regarding common reaction paths can be formulated. To calculate these values, representing traces were chosen based on signal strength, overlaps, and possible saturation effects.

E Proton-Transfer Reaction Mechanisms

We look at three different types of protons even though we only used hydroxonium as primary ion in our studies. According to the device manufacturer the ions generated are 97.56% H_3O^+ with contaminations of 1.95% O_2^+ and 0.49% NO⁺. [6]. Proton transfer vai H_3O^+ is still the dominating mechanism of course and ionization via NO⁺ was not considered in this study since it has the lowest concentration and would not provide additional insight for any of the documented species listed in E.1.2.

E.1 Literature Data

There is a large body of data available on reaction rates and product ratios for ionizing small organic molecules via H_3O^+ , O_2^+ , and NO^+ . The underlying studies were for the most part carried out within a selected-ion flow-tube (SIFT) mass spectrometer with a quadrupole analyser and not in a PTR-MS with time of flight analyser (TOF) as used in this study. For this reason, reaction rate constants calculated in these studies cannot be directly applied which makes direct quantitative calculations and comparisons were costly. In this study we therefore do not report concentrations but compare signal trends qualitatively - between different traces originating from the same species and between experiments of different applied potentials within the same trace. Moreover, if we have a vague idea of reaction rate constants (within reactions of a single product) we can compare orders of magnitude - for example between H_3O^+ and O_2^+ reaction of a species under consideration of the primary ion concentration and contamination.

E.1.1 Comparability with SIFT data

As mentioned above, a few important caveats apply to the applicability of data gathered from SIFT studies:

- It is specific to the reduced field strength E/N (in our case: E/N = 114Td autocalculated from drift tube temperature, voltage and pressure [6]). For example, fragmentation depends heavily on it [15].
- Measurements done by PTR-MS and SIFT-MS are not directly comparable. For example, less clusters with water are observed for PTR-MS [19].
- Following the drift chamber our setup includes a funnel and a lens leading to the TOF sensor. Additional reactions of ions and fragmentation might take place there, see E.3.
- Since we do not dilute the analyte, some of the species have very large concentrations outside the dynamic range of the PTR-MS. This leads to saturation effects described in E.2.

E.1.2 SIFT mechanism data

Tab. S34 lists all small organic compounds for which SIFT reaction data was available and have therefore been taken into account for species identification.

Table S34: List of different species with publically available data on ionization products.

speci	es chemical formula			<i>-</i>
sum	structure	species name	reference	comment
H_2O		water	[20]	
CH ₄	CH_4	methane	[10]	No reaction with H_3O^+ observed
C ₂ H ₆	C ₂ H ₆	ethane	[10]	No reaction with H ₃ O ⁺ observed
C ₃ H ₈	C ₃ H ₈	propane	[10]	No reaction with H ₃ O ⁺ observed
Cillia	n C.H.o	butane	[14]	No reaction with H_3O^+ observed
$C_4 \Pi_{10}$	II-C4H10	butane	[10]	Reaction with very small rate observed
CiHio	i-C. H.o	isobutane	[14]	No reaction with H ₃ O ⁺ observed
C41110	1-041110	isobutane	[10]	Reaction with very small rate observed
C5H12	n-C ₅ H ₁₂	pentane	[14]	No reaction with H_3O^+ observed
C5H12	i-C ₅ H ₁₂	isopentane	[14]	No reaction with H_3O^+ observed
C ₆ H ₁₄	n-C ₆ H ₁₄	hexane	[14]	
C ₈ H ₁₈ O	n-C ₈ H ₁₈ O	octane	[14]	
C10H22	$n-C_{10}H_{22}$	decane	[14]	
C ₃ H ₆	c-C ₃ H ₆	cyclopropane	[10]	
C_2H_4	C_2H_4	ethylene	[10]	
C ₃ H ₆	C ₃ H ₆	propylene	[10]	
C ₄ H ₈	CH ₃ CHCHCH ₃	2-butene	[10]	
C5H10	CH ₂ CHC ₃ H ₇	1-pentene	[14]	
C5H10	(CH ₃) ₂ CCHCH ₃	2-methyl-2-butene	[14]	
C ₃ H ₄	C ₃ H ₄	allene	[10]	
C_5H_8	CH ₂ CCHCH ₂	isoprene	[14]	
C ₂ H ₂	C ₂ H ₂	acetylene	[10]	
C ₃ H ₄	C ₃ H ₄	propyne	[10]	
C_4H_2	C_4H_2	diacetylene	[10]	
CH_4O	CH ₃ OH	methanol	[13]	products for different humidities
C ₂ H ₆ O	C ₂ H ₅ OH	ethanol	[13]	products for different humidities
			[15]	products for different field strengths
СНО	СЧОЧ	1 propagal	[13]	
C31180	03117011		[20]	products for different humidities
CaHaO	CHACHAOHCHA	2-propanol	[13]	
031180	engenzoneng	2-propanor	[15]	products for different field strengths
C4H10O	n-C4H0OH	1-butanol	[13]	
041100	ii eqiişeli	1 butunoi	[20]	products for different humidities
$C_4H_{10}O$	i-C ₄ H ₉ OH	2-methyl-1-propanol	[13]	
$C_4H_{10}O$	CH ₃ CH ₂ OHC ₂ H ₅	2-butanol	[13]	
$C_4H_{10}O$	t-C ₄ H ₉ OH	2-met-2-propanol	[13]	
C5H12O	C5H11OH	1-pentanol	[13]	
			[20]	products for different humidities
C ₅ H ₁₂ O	1-C5H11OH	3-met-1-butanol	[13]	
C ₅ H ₁₂ O	$C_2H_5CH_2OHC_2H_5$	3-pentanol	[13]	
$C_5H_{12}O$	$t-C_5H_{11}OH$	2-met-2-butanol	[13]	
$C_6H_{14}O$	C ₆ H ₁₃ OH	1-hexanol	[13]	products for different humidities
C ₈ H ₁₈ O	C ₈ H ₁₇ OH	1-octanol	[13]	
C ₈ H ₁₈ O	CH ₃ CH ₂ OHC ₆ H ₁₃	2-octanol	[13]	
C ₆ H ₆ O	C ₆ H ₅ OH	phenol	[13]	
C ₂ H ₆ O ₂	CH ₂ OHCH ₂ OH	1,2-ethanediol	[21]	
$C_3H_8O_2$	CH ₂ OHCHOHCH ₃	1,2-propanediol	[21]	
$C_3H_8O_2$	CH ₂ OHCH ₂ CH ₂ OH	1,3-propanediol	[21]	
$\overline{C_4H_{10}O_2}$	CH ₂ OHCHOHC ₂ H ₅	1,2-butanediol	[21]	
$C_4H_{10}O_2$	CH ₂ OHCH ₂ CHOHCH ₃	1,3-butanediol	[21]	
$C_4H_{10}O_2$	CH ₂ OHC ₂ H ₄ CH ₂ OH	1,4-butanediol	[21]	
C ₅ H ₁₂ O ₂	CH ₂ OHC ₃ H ₆ CH ₂ OH	1,5-pentanediol	[21]	

C5H10O2	c-CHOHCHOHC ₃ H ₆	1.2-cyclopentanediol	[21]	
CH ₂ O	НСНО	formaldehvde	[9]	
C ₂ H ₄ O	CH ₃ CHO	acetaldehvde	[9]	
C3H6O	C ₂ H ₅ CHO	propanal	[9]	
<u> </u>			[9]	
C_4H_8O	C ₃ H ₇ CHO	butanal	[17]	in agreement with earlier study
C ₄ H ₈ O	(CH ₃) ₂ CHCHO	isobutanal	[17]	
C ₅ H ₁₀ O	C ₄ H ₉ CHO	pentanal	[9]	
C ₅ H ₁₀ O	(CH ₃) ₂ CHCH ₂ CHO	isopentanal	[17]	
C ₆ H ₁₂ O	C ₅ H ₁₁ CHO	hexanal	[9]	
C ₇ H ₁₄ O	C ₆ H ₁₃ CHO	heptanal	[17]	
C ₉ H ₁₈ O	C ₈ H ₁₇ CHO	octanal	[17]	
C ₁₀ H ₂₀ O	C ₉ H ₁₉ CHO	decanal	[17]	
C ₇ H ₆ O	C ₆ H ₅ CHO	benzaldehyde	[9]	
C ₃ H ₄ O	CH ₂ CHCHO	propenal	[9]	
C ₄ H ₆ O	CH ₃ CHCHCHO	2-butenal	[17]	
C5H8O	t-C ₂ H ₅ CHCHCHO	trans-2-pentenal	[17]	
C5H8O	t-CH ₃ CHC(CH ₃)(CHO)	trans-2-methyl-2-butenal	[17]	
C6H10O	C ₃ H ₇ CHCHCHO	trans-2-hexenal	[9]	
C6H10O	C ₂ H ₅ CHCHCH ₂ CHO	cis-3-hexenal	[9]	
C7H12O	t-C4H0CHCHCHO	trans-2-heptenal	[17]	
C ₈ H ₁₄ O	t-C5H11CHCHCHO	trans-2-octenal	[17]	
CoH160	t-C ₆ H ₁₂ CHCHCHO	trans-2-nonenal	[17]	
C5H ₂ O ₂	CHOC ₂ H ₆ CHO	1.5-pentanedial	[9]	
$\frac{C_3H_8O_2}{C_2H_4O_2}$	СНаОНСНО	glycoaldehyde	[15]	products for different field strengths
0211402		grycourdenyde	[10]	products for different field strengths
C_3H_6O	CH ₃ COCH ₃	acetone	[16]	products for different humidities
			[0]	products for different numberies
C_4H_8O	CH ₃ COC ₂ H ₅	2-butanone	[16]	products for different humidities
			[10]	products for different numerics
$C_5H_{10}O$	CH ₃ COC ₃ H ₇	2-pentanone	[16]	products for different humidities
CeH10O	CalleCOCalle	3-pentanone	[0]	products for different numberies
C5H100	$(CH_2)_2CHCOCH_2$	3-methyl-2-butanone	[16]	products for different humidities
031100	(013)2011000113	5 montyr 2 outanone	[10]	products for different numberies
$C_6H_{12}O$	CH ₃ COC ₄ H ₉	2-hexanone	[16]	products for different humidities
			[9]	
$C_6H_{12}O$	$C_2H_5COC_3H_7$	3-hexanone	[16]	products for different humidities
C6H12O	$CH_3COCH(CH_3)(C_2H_5)$	3-methyl-2-pentanone	[16]	products for different humidities
C6H12O	(CH ₃) ₂ CHCH ₂ CCH ₃	4-methyl-2-pentanone	[16]	products for different humidities
$\frac{C_{0}C_{12}}{C_{7}H_{14}O}$	CH ₃ COC ₅ H ₁₁	2-heptanone	[16]	products for different humidities
$\frac{C_7 H_{14} O}{C_7 H_{14} O}$	C2H5COC4H0	3-heptanone	[16]	products for different humidities
C ₈ H ₁₆ O	C2H5COC5H11	3-octanone	[16]	products for different humidities
CoH100	CH ₂ COC ₇ H ₁₅	2-nonanone	[16]	products for different humidities
C10H20O	CH ₂ COC ₂ H ₁₇	2-decanone	[16]	products for different humidities
- 10 20 -			[9]	r
$C_4H_6O_2$	CH ₃ COCOCH ₃	2,3-butanedione	[16]	products for different humidities
C5H8O2	CH ₃ COCOC ₂ H ₅	2.3-pentanedione	[16]	products for different humidities
C6H10O2	CH ₃ COCOC ₃ H ₇	2.3-hexanedione	[16]	products for different humidities
C4H6O	CH ₃ COC ₂ H ₃	3-buten-2-one	[16]	products for different humidities
C5H8O	CH ₃ C(CH ₂)(COCH ₃)	3-methyl-3-buten-2-one	[16]	products for different humidities
C6H10O	$\frac{C_2H_4C(CH_3)(COCH_3)}{C_2H_4C(CH_3)(COCH_3)}$	3-methyl-3-penten-2-one	[16]	products for different humidities
C6H100	(CH ₃) ₂ CCHCOCH ₂	4-methyl-3-penten-2-one	[16]	products for different humidities
CaHaO	C6H5COCH3	acetophenone	[16]	products for different humidities
C _e H _e O	C6H5COCH2	1-phenylethanone	[9]	r
C2H4O2	HCOOCH ₃	methyl formate	[18]	
C3H6O2	HCOOC ₂ H ₅	ethyl formate	[18]	
C3H6O2	CH ₃ COOCH ₂	methyl acetate	[18]	
- 30.02			[18]	
$C_4H_8O_2$	CH ₃ COOC ₂ H ₅	ethyl acetate	[15]	products for different field strengths
C ₄ H ₈ O ₂	C2H5COOCH3	methyl propionate	[18]	1 and a second and a second and
C4H802	C2H5COOC2H5	etyhyl propionate	[18]	
C5H10O2	C ₃ H ₇ COOCH ₃	methyl butanoate	[18]	
C ₈ H ₈ O ₂	C ₆ H ₅ COOCH ₃	methyl benzoate	[18]	
C4H10O	C2H5OC2H5	diethyl ether	[12]	
C5H100	C3H5OC2H5	allyl ethyl ether	[12]	
- 5100			LJ	

C ₅ H ₁₂ O	C ₄ H ₉ OCH ₃	butyl methyl ether	[12]	
C ₆ H ₁₄ O	C ₂ H ₅ C(CH ₃) ₂ OCH ₃	tertiary pentyl methyl ether	[12]	
C ₆ H ₁₄ O	C(CH ₃) ₃ OC ₂ H ₅	butyl ethyl ether	[12]	
C ₆ H ₁₄ O	C ₃ H ₇ OC ₃ H ₇	dipropyl ether	[12]	
C ₆ H ₁₄ O	(CH ₃) ₂ CHOCH(CH ₃) ₂	diisopropyl ether	[12]	
$C_4H_{10}O_2$	CH ₃ OC ₂ H ₄ OCH ₃	ethylene glycol dimethyl ether	[12]	
C ₄ H ₈ O		tetrahydrofuran	[12]	
C ₇ H ₈ O	C ₆ H ₅ OCH ₃	anisole	[12]	
CHaOa	НСООН	formic acid	[18]	
011202	пеобл	Torrine acid	[15]	products for different field strengths
Callina	CHACOOH	acetic acid	[18]	
0211402	engeoon		[15]	products for different field strengths
$C_3H_6O_2$	C ₂ H ₅ COOH	propionic acid	[18]	
$C_4H_8O_2$	C ₃ H ₇ COOH	n-butyric acid	[18]	
$C_4H_8O_2$	(CH ₃) ₂ CHCOOH	iso-butyric acid	[18]	
C5H10O2	C ₄ H ₉ COOH	valeric acid	[18]	
C5H10O2	(CH ₃) ₃ CCOOH	trimethylacetic acid	[18]	
$C_3H_4O_2$	CH ₂ CHCOOH	acrylic acid	[18]	
C ₃ H ₆ O ₃	CH ₃ CHOHCOOH	lactic acid	[18]	
C ₆ H ₆	C ₆ H ₆	benzene	[14]	
C ₇ H ₈	C ₆ H ₅ CH ₃	toluene	[14]	
C8H10	C ₆ H ₅ C ₂ H ₅	ethylbenzene	[14]	
C ₈ H ₁₀	o-C ₆ H ₅ CH ₃ CH ₃	ortho-xylene	[14]	
C8H10	m-C ₆ H ₅ CH ₃ CH ₃	meta-xylene	[14]	
C8H10	p-C ₆ H ₅ CH ₃ CH ₃	para-xylene	[14]	

E.1.3 Proton Affinities

For species without SIFT data available or where ionization via H_3O^+ is not reported, assessing the proton affinity can be helpful. It is defined as the negative enthalpy change at protonation and in comparison to the proton affinity of water is a measure of how likely a proton transfer from H_3O^+ is. A proton affinity smaller than water does not necessarily mean that there is no ionization via H_3O^+ at all though: Firstly, protonation can still occur - as it is just a matter of probability - if the proton affinity is not much smaller and the analyte is present in substantial concentration. Secondly, cluster forming via H_3O^+ is possible as was observed for multiple species and documented in E.3.

Table S35: Proton affinities (PA) at room temperature (T = 300 K) and mean elution times (ET) observed for described species. Water is used as a reference, all values below are highlighted in red and values only slightly above are highlighted in yellow.

Observed species	$ $ PA $[kJmol^{-1}]$	ET [min]	Comment
water	691		from [22]
carbon monoxide	594	2.2	from [22]
methane	552	2.9	from [22]
carbonic acid	741	3.8	from [23]
carbon dioxide	541	3.9	from [22]
ethylene	681	5.6	from [22]
methanol	725	7.1	from [22]
formaldehyde	712	7.2	from [22]
propylene	752	9.1	from [22]

acetaldehyde	769	10.5	from [22]
ethanol	776	11.9	from [22]
1-butene	802	12.0	from [22]
butadiene	783	12.2	from [22]
trans-butene	747	12.4	from [22]
cis-butene	pprox 747	12.7	assumed similar to diastereomer
cyclopropane	750	13.1?	from [22]
propanal	786	14.5	from [22]
acetone	812	15.3	from [22]
allyl-alcohol	750 to 850	16.5	assumed similar to structural isomers
1-pentene	≈ 809	16.9	assumed similar to positional isomer
propanol	787	17.2	from [22]
2-pentene	809	17.3?	from [22]
butanedione	802	20.5	from [22]
crotyl alcohol	750 to 850	20.8?	assumed similar to structural isomers
butanone	827	21.6?	from [22]
butanal	793	21.9	from [22]
ethyl-acetate	836	23.3	from [22]
2,3-pentanedione	≈ 874	36.9	assumed similar to positional isomer
2,4-pentanedione	874	39.0	from [22]

E.2 Saturation Effects

If some species have a very large concentration (outside of the dynamic range of the instrument), specific effects start to occur. It is important to identify these effects and assess their severity so they can be handled accordingly. For all species affected, it is included in the discussion in D accordingly.

E.2.1 Primary Ion depletion

If the ionization rate of a species via a specific primary ion is very large - due to large concentration of the species and/or high reaction rate constant (RRC) - the primary ion concentration can drop noticeably and is no longer orders of magnitude greater than any secondary ion detected. This has two direct consequences:

- 1. The concentration of primary ions can no longer be assumed to be constant. Considering the rate equation $\frac{d[MH^+]}{dt} = k_C [M] [H_3O^+]$ for protonation $M + H_3O^+ \longrightarrow MH^+ + H_2O$, even if the RRC k_C is constant, the reaction rate (aka counts per second) is no longer a direct measure for analyte concentration [M]. Relative Faradaic Efficiencies calculated for these data points are therefore skewed.
- 2. Now, secondary ions (aka protonated species) are at similar or even higher concentrations as primary ions ($[MH^+] \approx [H_3O^+]$). Thus, they are now likely to hit unionized species to form large clusters at an observable rate, see E.2.2.

For these reasons, substantial drops in PI concentration were identified and applied to species via their observed elution times. Tab. S36 lists all species for which primary ion depletion of either H_3O^+ or O_2^+ was verified, details shown further below. To circumvent or reduce the effects of PI depletion listed above, for these species the products of ionization via residual O_2^+ should be analysed in detail. Alternatively, trends of cluster-forming can be roughly quantified as discussed in E.2.2.

Table S36: Detected species that verifiably caused depletion of primary ions in some of the experiments.

Ionization		Applied potential U _{Hg/HgO} [mV]								
Species	PI	2000	2500	3000	3500	4000	4500	5000		
Ethylene	O_2^+		full	full	full	full	full			
	H_3O^+		partial	full	full	partial				
Propylene	H_3O^+		full	full	partial					
Acetaldehyde	H_3O^+		full	full	full	full	full	full		
Ethanol	H_3O^+					partial	partial	partial		
Propanal	H_3O^+		partial							

Drop in hydronium ions was analysed via Fig. S47. Unfortunately, the trace representing H₃¹⁶O⁺ (m/z = 19.05 Da) cannot be used for assessment of PI depletion since the detector is saturated (see E.2.3). We therefore used m/z = 21.02 Da which is corresponding with low-abundance oxygen isotope H₃¹⁸O⁺. Fig. S47(b) shows somewhat varying baseline signals for the different measurements. For this reason, depletion was assessed via signals normalized to the median intensity throughout the course of an experiment, see Fig. S47(a). The usual noise levels can be seen around 15% to 20%, so the threshold for partial PI depletion was set to 25% deviation from the median.



S47(a): Smoothed signal relative to median for different U_{Hg/HgO}



S47(b): Smoothed signal for different UHg/HgO

Figure S47: XIC of $H_{3}^{18}O^{+}$ trace.

As a few species cause such an extreme drop in PI concentration that we must assume no further protonation via PI at this point, full depletion was defined for drop below 50% of the median. Since the average signal of the experiment at $U_{Hg/HgO} = 5V$ is considerably smaller, similar absolute standard deviations are account for significantly larger relative noise levels. For this reason, a drop below the according threshold in this experiment was only considered as partial or full depletion in Tab. S36 if it fit the trend of production rates at this retention time.

Drop in oxygen ions was analysed via Fig. S48. Analogous to H_3O^+ , the low-abundance oxygen isotope ${}^{16}O^{18}O^+$ (m/z = 33.99 Da) was used instead of ${}^{16}O_2^+$ for PI depletion assessment. As the signals depcited in Fig. S48(b) are quite small, relative noise levels are quite large and only substantial drops of intensity levels were considered. Again, the signal was normalized by the median but as intensity levels are similar here throughout experiments, this does not change the picture much in Fig. S48(a): Full PI depletion was now defined for any signal dropping below 30% of the median.



S48(a): Smoothed signal relative to median for different U_{Hg/HgO}



S48(b): Smoothed signal for different U_{Hg/HgO}

Figure S48: XIC of ${}^{16}O {}^{18}O^+$ trace.

E.2.2 Cluster forming

As a direct consequence of (partial or full) PI depletion, PTR mechanisms might change and therefore products and product fractions. For example, detected fragmentation can be reduced as fragments themselves act as proton donors in secondary proton transfer reactions or temperature conditions change. [24] This would mean that product ratios change towards fewer fragments in favour of directly protonated species. Comparing relative integrated intensities of MH⁺ with fragments such as MH⁺–CH₄, this effect would show up as broadened curves for the fragment - flatter around the peak as its product ratio is smallest for peak production.

Caused by the same fact of more collisions between unionized species with secondary products, we mostly observe a different effect in this study: Clusters between unionized species and either protonated species or fragments thereof are forming and are stable enough to be detected as large ions, see E.3. The larger these clusters get, they will be subject to increased fragmentation which leads to signals for a multitude of traces/masses. These effects have been identified as a problem in the analysis of alcoholic compounds where PI depletion via ethanol protonation, cluster forming and subsequent fragmentation precludes monitoring of some minor species that should appear at the same masses. [25] This is one of the reasons why product separation via GC column was done in this study.

The observed clustering should increase with concentration of the respective species and can therefore help with identification and quantification [24]. Relative integrated intensities of traces representing clusters should show steeper curves than those representing simply protonated species. Relative to a sharp peak, the relative integrated intensities should be smaller for all other applied potentials as its product ratio is smallest for the lowest production rate.

We can explore the relative trends mentioned above by comparing secondary ions detected for species that cause PI depletion as in Fig. S49. In Fig. S49(a) we compare the relative integrated intensities of the main secondary ion via PTR $C_2H_4 + H_3O^+ \longrightarrow C_2H_5^+ + H_2O$ with its directly related tertiary ions via fragmentation $C_2H_5^+ - H_2 \longrightarrow C_2H_3^+$ and clustering $C_2H_5^+ + C_2H_4 \longrightarrow C_4H_9^+$ (full mechanism see E.3.2). As expected, the curve representing the signal from the cluster has a much sharper curve that is below the secondary ion. Meanwhile, the curve representing the signal of the fragment coincides with that of the secondary ion within one standard deviation for $U_{Hg/HgO} \leq 3.5 V$. For bigger applied potentials, it is slightly above - indicating a flatter shape as expected through secondary proton transfers. Overall, this effect seems to be less pronounced for the conditions used in our experiments: in Fig. S49(b) the "fragmentation 2" curve is also only slightly above or on the curve of the secondary ion within one standard deviation. Here we compare the main secondary ion of propylene via PTR $C_3H_6 + H_3O^+ \longrightarrow C_3H_7^+$ and its direct tertiary ion via fragmentation $C_3H_7^+ - H_2^+ \longrightarrow C_3H_5^+$ (as "fragmentation 1") with the secondary ion's direct tertiary ions via clustering $C_3H_5^+ + C_3H_6 \longrightarrow C_6H_{11}^+$ and fragmentation $C_3H_5^+ - H_2 \longrightarrow C_3H_3^+$ (as "fragmentation 2"). For the full mechanism, see S53.



S49(a): Ethylene: protonated species $C_2H_5^+$ vs. di- S49(b): Propylene: protonated species $C_3H_7^+$ and rectly related fragment $C_2H_3^+$ and cluster $C_4H_9^+$ its direct fragment 1 $C_3H_5^+$ vs. derived cluster $C_6H_{11}^+$ fragment 2 $C_3H_3^+$

Figure S49: Relative intensities of traces related to products that cause primary ion depletion. Comparison of trends between protonated species, fragments, and clusters.

E.2.3 Detector saturation

The TOF analyser has a detection limit of counts per second that seems to be $\approx 1 \times 10^5 \, \text{s}^{-1}$ as this is the maximum intensity detected for the primary ion H_3O^+ . We know the actual concentration to be larger as the H_3 ¹⁸O⁺ signal is around 500 s⁻¹ on average which represents an isotope of 0.2% natural abundance which would warrant a H_3 ¹⁶O⁺ signal of up to $3 \times 10^5 \, \text{s}^{-1}$. This postulated detection limit is not constantly reached by

the primary ion as it largely depends on the curve fit over m/z dimension: baselines vary across measurements and also change within the same measurement. Because of this, an even larger signal of H₃O⁺ might be detected at times of PI depletion since changing curve shapes can change the fitting parameters - this is the reason we need to look at the signals of less-abundant isotopes to assess PI depletion.



Figure S50: Comparison of the traces with the largest signals for different applied potentials in order to check for detector saturation.

In order to check for detector saturation for any of the other masses used for product anal-

ysis analysis, the four traces with the largest peak signals were compared to the primary ion in Fig. S50. All of these traces at some point have signals larger than the primary ion - namely for ethylene, propylene, acetaldehyde and propanal. Intensities larger than that of the primary ion trace do not necessarily mean detector saturation was reached, but it is a strong indicator. Additionally, in some instances (e.g. $C_2H_5O^+$ at $t_{CH_3CHO} = 10.5$ min for $U_{Hg/HgO} = 3.5$ V) a signal drop in the middle of the peak can be seen - a clear sign that the detector could no longer count the corresponding masses hitting the sensor.

The qualitative trends of masses represented by traces with potential detector saturation need to be measured by some alternative trace representing another mass connected to the same product under assessment. Ideally, we just use the corresponding ¹³C isotopes as other traces might show different trends as explained in E.2.2. In some cases we might even be able to use oxygen isotopes ¹⁸O as we did for PI depletion assessment in E.2.1.

E.3 New reactions and fragments

There are three types of additional reactions found:

- 1. Clustering with unionized version (for large concentrations, see E.2.2)
- 2. Cluster with hydronium as additional protonation product: In the literature this is rather often interaction with humidity but our device is designed in a way to minimize this and we have good separation of water (except for D.3 and D.5). Forming of hydronium clusters
- 3. Dissociation of (usually stable) species

In the following, PTR mechanisms of species with a number of newly found reactions and fragments are sketched out. Blue reaction arrows represent high certainty while orange means some uncertainties are remaining.

E.3.1 Methane

The mechanism in Fig. S51 shows confirmation of exclusive O_2^+ ionization due to the small proton affinity of methane. Other than in SIFT-MS studies [10], we observed substantial fragmentation of the formed $CH_3 \cdot O_2^+$ cluster.

E.3.2 Ethylene

For very large ethylene concentrations, a majority of C_2H_4 molecules is not ionized, we can see a drop in both primary ions as well (see E.2.1). At this point, protonated ethylene reacts further with unprotonated ethylene via the mechanism described in Fig. S52.

In Fig. S52 we see all the documented PTR reactions as per SIFT-MS studies [10] as well as all newly observed secondary reactions leading to tertiary ions etc. but even additional


Figure S51: Suggested PTR mechanism for methane.



Figure S52: Suggested PTR mechanism for ethylene.

secondary ions $C_2H_4 \cdot H_5O_2^+$ and $C_2H_4 \cdot O_2^+$. Signal fractions are calculated via sampling (as described in C.3.2) and the values shown are estimated averages across applied potentials. It has to be noted though that since many of these ions depend on significant PI depletion and therefore ethylene concentration, variance can be large.

E.3.3 Propylene

In Fig. S53 we see very similar effects for propylene ionization as for the ethylene described in E.3.2: Additional secondary ion via $C_3H_6 + H_3O^+ \longrightarrow C_3H_9O^+$ has been established along with a range of tertiary ions caused by fragmentation (partially dependent on reduced field in drift chamber) and clustering (mostly due to large propylene concentration and PI depletion).



Figure S53: Suggested PTR mechanism for propylene.

The mechanism towards a few of the detected species remains unclear - especially if signals are very small (which makes it hard to compare trends as uncertainties are large) or if their signals are much larger than supposed "upstream" species. The latter case occurs for example with large signal of $C_2H_3O^+$ compared to small $C_3H_9O^+$ and barely detectable $C_2H_5O^+$ signal. This can be explained though if secondary and tertiary ions are unstable and e.g. fragmentation has a larger reaction rate constant than initial ionization.

E.3.4 Acetaldehyde

Fig. S54 shows the compiled mechanism of acetaldehyde ionization witnessed in the PTR-MS experiments conducted. Again there is an additional secondary ion via H_3O^+ cluster forming and a few other tertiary ions but it is interesting to note that even though it is probably the species that leads to the most protonation (see PI depletion in E.2.1), we do not see much clustering with existing acetaldehyde as we do for ethylene in S52. The reason is probably that $C_2H_5O^+$ does not protonate nearly as well as hydronium ions (condition for significant rate of secondary reactions is $[MH^+] \gtrsim k_1/k_2 [H_3O^+]$ where k_1 is RRC for $M + H_3O^+ \longrightarrow MH^+ + H_2O$ and k_2 is RRC for $MH^+ + M \longrightarrow M_2H^+$).



Figure S54: Suggested PTR mechanism for acetaldehyde.

The $C_2H_5O_2^+$ signal seems to be an artefact at first glance but is ultimately verified as acetaldehyde ionization product, see discussion in D.7. The exact mechanism remains unclear due to lack of comparability.

E.3.5 Ethanol

Fig. S55 shows the mechanism of ethanol ionization witnessed. Compared to a study analysing alcoholic beverages via PTR-MS [25] we see the same main responses: secondary ion $C_2H_7O^+$ and tertiary ion $C_2H_5^+$ making up a slightly higher percentage than in the literature. Also, $C_2H_9O_2^+$ is observed with a significantly larger signal fraction which is probably caused by different origins - while the humidity in the literature experiment causes clustering of secondary ion with water, the larger field strength in our experiment makes this another secondary ion.



Figure S55: Suggested PTR mechanism for ethanol.

Clustering with unionized species to form $C_4H_{13}O_2^+$ is observed in our experiments at a much smaller scale as ethanol concentration is definitely smaller than the 10 vol-% in the literature [25]. The mentioned study does not report any of the other fragments reported at signal fractions smaller than 1% here. Furthermore, no $C_2H_5O^+$ is reported. This could be interpreted as evidence for O_2^+ origin (since residual primary ion ratios would have differed) but could also plainly be caused by the smaller reduced field strength leading to less fragmentation.

E.3.6 Propanol

The documented main O_2^+ product CH_3O^+ [13] was not detected - most likely due to overlap with the primary ion. The two documented protonation products $C_3H_7^+$ and $C_3H_9O^+$ [13] were found but in a different ratio as the $C_3H_7^+$ signal is multiple orders of magnitude larger. This is consistent with increased fragmentation experienced in our system compared to most of the referenced SIFT studies. For this reason, a few traces resulting from even further fragmentation were found - one of them ($C_3H_5^+$) with a significant signal strength. Moreover, a H_3O^+ cluster was found.



Figure S56: Suggested PTR mechanism for propanol.

E.3.7 Propanal

For propanal, none of the reported O_2^+ products [9] were detected - concentrations were probably too small to lead to any significant protonation by small amounts of residual oxygen primary ions. A few other protonation products apart from the reported $C_3H_7O^+$ [9]: again, a cluster with H_3O^+ was found as well as a few fragments due to dissociation from the seconary ions.



Figure S57: Suggested PTR mechanism for propanal.

As the very small signal at $m/z \approx 64$ Da could not be assigned with a reasonable degree of certainty as documented in D.11, it is not shown here.

E.3.8 Ethyl acetate

For acetaldehyde our observations lined up very closely with a previous PTR-MS study reporting secondary ions and their ratios for different reduced field strengths [15]. The signal ratios of the major ions $C_4H_9O_2^+$, $C_2H_5O_2^+$, and $C_2H_3O^+$ were very close to the ratios reported for $E/N \approx 113$ Td at the smallest relative humidity. Extrapolating the data to even smaller humidities, the values come even closer to what was observed in this study. Moreover, the only minor secondary ion reported independent of humidity, $C_4H_{11}O_3^+$ was also observed along with two of its unreported fragments, $C_2H_7O_3^+$ and $C_4H_{11}O_2^+$.



Figure S58: Suggested PTR mechanism for ethyl acetate.

F Verification Experiments

For verification purposes, three additional GC-MS experiments were conducted. The setup of the flow cell was slightly changed for each one (gas inlet or catalyst material respectively). Measurements and data analysis were carried out in the same fashion as the main experiments.

F.1 Experimental Details

F.1.1 Setup and measurements

Inert gas experiment: In order to determine that no detected products are due to contamination of the cell or the GC column and verify the baseline signals during column heating, we performed sampling of potential gaseous products formed on the copper electrode in the presence of inert gas only. Nitrogen (instead of carbon dioxide) was passed through the electrochemical cell equipped with the copper-based GDE. The cell was running at $1.5 \,\mathrm{A \, cm^{-2}}$ without any presence of CO₂. After 5 min of the reaction the gas sample was inserted into GC and GC-MS was recorded.

Pure carbon paper experiment: In order to determine that no detected products formed in the GDE independent of the copper catalyst (so either by non-metal-based reduction of CO_2 or non-electrochemical reactions in the electrolyte), we performed sampling of gaseous products formed on pure carbon paper in the presence of carbon dioxide. CO_2 was passed through the electrochemical cell equipped with carbon paper and the cell was running at $1.5 \,\mathrm{A \, cm^{-2}}$. After 5 min of the reaction the gas sample was inserted into GC and GC-MS was recorded. As no eCO2R is observed in this experiment, the detected CO_2 signal can serve as a starting point for some discussions regarding absolute yields, see section G.

Carbon-13 isotope experiment: In order to determine that all detected products originate from CO_2 reduction (instead of a different carbon source), a single run with ${}^{13}CO_2$ was performed at a constant current density of $1.5 \,\mathrm{A \, cm^{-2}}$. It was carried out and measured analogous to the other experiments described. Additional traces were extracted to verify specific compounds as mentioned in appendix D.

F.1.2 Constraints imposed on comparability

When comparing these reference experiments with the original measurements or with each other, a few important caveats apply that need to be considered carefully. The most important one concerns applied potentials and corresponding currents: while using applied or corrected potentials as control variable is already inherently problematic for highcurrent GDEs (see section A), current densities are also limited for comparing these reference experiments as only HER drives this current in the experiments with inert gas and carbon paper respectively. Furthermore, the change of the setups and electrodes as well as assembly and cleaning procedures causes natural variations to be larger compared to the original measurements. For example, this can lead to slightly different retention times observed in our reference experiments, which is also influenced by cross-interactions between products.

F.2 Post-processing verification

For species analysis shown in appendix D, the signal data collected by PTR-MS is processed. The processing steps are described in detail in appendix C.3 and shall be verified.

F.2.1 Baseline subtraction

One important aspect of data processing is the dynamic subtraction of baseline signals as some signals exhibit quite substantial baseline signals that vary significantly across time. For the dynamic subtraction to be valid, its origin needs to be systematic and unrelated to eCO2 products.

As explained in appendix B.1, the observed signal plateaus are thought to be caused by GC column heating and some accompanying stationary phase disintegration as the heating protocol coincides very well with the signal plateaus observed. Indeed, the same signal plateaus are observed within the N_2 experiment shown in Fig. S59, confirming a non-CO₂-related origin.



Figure S59: XIC for $C_5H_9^+$ trace (m/z = 69.07 Da) of different eCO2R experiments compared to verification measurement with nitrogen.

Subtracting the baseline signal is not only valid but actually necessary to assess production trends across applied potentials for two reasons: First, a constant error in signal strength

will distort computed rFE values. Second, absolute values of baseline signals will vary somewhat across different measurements.

To illustrate this, we consider an even more extreme case: the comparison of ${}^{12}\text{CO}_2$ to ${}^{13}\text{CO}_2$ experiments as different masses with different baseline signals need to be assessed. In Fig. S60 this is done for 2,4-pentanedione. As $m/z = 101.06 \text{ Da} ({}^{13}\text{C}_5\text{H}_9\text{O}_2^+)$ exhibits a significant baseline signal while $m/z = 106.07 \text{ Da} ({}^{12}\text{C}_5\text{H}_9\text{O}_2^+)$ does not, the signal ratios differ greatly without baseline subtraction. While signal ratios might vary slightly (especially for very large product concentrations as discussed in appendix E.2), they are generally expected to be very similar for the same product of moderate concentration across experiments. Indeed, when baseline subtraction is applied, it is the case. Compared to subtracting a minimum value, when subtracting a computed baseline that takes trends into account as explained in appendix C.3, values are even more similar. This is explained by improved deconvolution of 2,3-pentanedione in this case.



S60(a): Extracted ion chromatograms.

S60(b): Signal ratios $I(C_2H_3O^+)/I(C_5H_9O_2^+)$

Figure S60: Comparison of main signals related to 2,4-pentanedione and their ratios between ${}^{12}\text{CO}_2$ experiment at J = 0.5 A and ${}^{13}\text{CO}_2$ experiment.

F.2.2 Signal integration

Another important aspect of data post-processing is the integration (or rather summation) of signals across peak width to calculate the peak area. This is usually done for absolute quantification purposes which does not play a major role in this work as we focus on relative trends (notwithstanding some rough estimates shown in appendix G). It still plays an important role as it reduces the influence of a single point of data and allows for the calculation of empirical standard deviations.

The effectiveness of this approach is indicated by the matching rFE values and trends calculated via integrated signals of different secondary and tertiary ions that correspond

to the same eCO2R product (especially corresponding isotopes) as shown throughout appendix D (excluding effects discussed in appendix E.2). The rFE values of the three traces related to butanedione shown in Fig. S40(b) for example only differ less than .5% from their common mean. Due to the robustness of this method to compare signals of different traces across measurements, we can even rely on it to distinguish species eluting at the same time - e.g., C_4H_8O isomers in appendix D.14.

In order to compare signals within the same measurement, a second approach has been introduced in appendix C.3.2 to calculate and compare signal fractions of different traces. In contrast to the former approach it needs to be stable across many orders of magnitude as some secondary or tertiary ions produced by the proton-transfer reaction are present only in small quantities while large analyte concentrations are measured. In Fig. S61 this is done for acetaldehyde - only traces with small to moderate signal strength are compared because saturation effects are observed for the main ion responses as discussed in appendix E.3.7. The ratios obtained by using peak values of the raw data, integrated raw signals, integrated smoothed signals, and sampled values according to appendix C.3.2 are shown. They are compared to a reference measurement on a acetaldehyde standard solution. It is apparent that signal integration yields results that are closer to the reference which can be attributed to flatter peaks of small signals. As some of these small signals do not exhibit a meaningful SNR over the full peak width which was determined by much larger signals, sampling closely around the maximum signal improves the data even more. The remaining differences can be attributed to other effects related to analyte concentration that are described at length in appendix E.



Figure S61: Bar graph comparing signal ratios calculated by different means of minor traces related to acetaldehyde. For reference, a standard solution was measured with PTR-MS.

In Fig. S61 it seems like signal filtering via moving average does not have much effect. The same can be observed for most derived values throughout all species analysed in appendix D. Smoothed signals were still used, mostly for visualisation aspects as it makes

it easier to assess ion chromatograms of small signals. Nonetheless, there still remains an advantage for using the smoothed signal also in data processing as outliers at specific points (especially start and end points of peak widths, t_1 and t_2 , see appendix C.3) are not over-interpreted.

F.3 Artefact verification

A few potential artefacts have been identified during species analysis as described in appendix D. These are revisited here and compared to the results of the verification experiments.

F.3.1 Mass 45 and propylene

As shown in appendix D.6, some odd peaks of $C_2H_5O^+$ can be observed close to propylene peaks. Within the ¹³C experiment, the $C_2H_5O^+$ trace, which appeared shifted against the rest of the propylene signal for ¹²C, seems to coincide perfectly with the main ion responses as shown in Fig. S62(a) at first glance. This is caused by the $C_3H_7^+$ ion though as masses only differ ≈ 0.02 Da. The subsequent small peak afterwards can be attributed to acetaldehyde as its huge concentration seems to cause a small peak and dip before the actual large signal peak as seen in Fig. S62(b).



S62(a): Relative signals of relevant traces within ¹³C experiment and indication of propylene retention time compared to peak of interest.



S62(b): Relative signals of relevant traces within different ¹²C experiments and indication of observed propylene retention timeframe.

Figure S62: Analysis of $C_2H_5O^+$ signal possibly related to propylene.

The lack of a similar peak within the N_2 and carbon experiments confirms that these are not systematic errors or artefacts related to the GC column or the GDE. On the other hand, the large baseline signals of the reference experiments show similarities with the peaks observed for smaller applied potentials in the original experiments and indicates those to be caused by GC heating.

F.3.2 Mass 61 and acetaldehyde

As shown in appendix D.6, some odd peaks of $C_2H_5O_2^+$ can be observed close to propylene peaks. Within the ¹³C experiment, the $C_2H_5O_2^+$ trace, which appeared shifted against the rest of the acetaldehyde signal for ¹²C, seems to coincide perfectly with the main ion responses as shown in Fig. S63(a). The signal is extremely small though and can only be distinguished clearly because, unlike its ¹²C isotope, the ¹³C₂H₅O₂⁺ trace does not exhibit a substantial baseline signal. This becomes obvious in Fig. S63(b) where reference experiment on carbon paper exhibits a similar signal - albeit smaller in absolute terms that only differs from the eCO2R experiments in minor ways. In conclusion, $C_2H_5O_2^+$ is likely produced via the PTR mechanism of acetaldehyde as described in appendix E.3.7, yet in such small amounts that it is barely distinguishable from the large baseline signal and therefore not quantifiable.



S63(a): Relative signals of relevant traces within carbon-13 experiment and indication of acetalde-hyde retention time.



S63(b): XIC of relevant traces within different carbon-12 experiments and indication of observed acetaldehyde retention timeframe.

Figure S63: Analysis of $C_2H_5O^+$ signal possibly related to propylene.

F.3.3 Mass 42 and cyclopropane

A peak of $C_3H_6^+$ that is described in appendix D.10 was originally hypothesised to be cyclopropane. This could be falsified via the reference experiments: Fig. S64(a) shows no significant ${}^{13}C_3H_6^+$ signal at the retention time expected for an eCO2R product based on the Δt experienced of other products. Not only is there just a very small peak without noticable SNR, a significant ${}^{12}C_3H_6^+$ peak is observed later, indicating a systematic effect.

This is confirmed in Fig. S64(b) as not only the experiment with CO_2 on carbon paper produces this artefact but also the experiment with nitrogen.



S64(a): $C_3H_6^+$ signals in ¹³C experiment and indication of expected retention time of cyclopropane.



S64(b): XIC of $C_3H_6^+$ signals observed across different ¹²C experiments.

Figure S64: Analysis of C₃H₆⁺ artefact observed across all experiments.

F.4 Species verification

All eCO2R products detected and described in appendix D were investigated through the reference experiments for verification. Only those which we relied on these experiments for verification and/or have not been reported prior to this study are discussed in detail below.

F.4.1 Butene isomers and butadiene

For verification of the different C₄ hydrocarbons reported in appendix D.9, corresponding secondary ions detected in the ¹³C experiment are shown in Fig. S65(a). All three C₄H₉⁺ peaks corresponding to different butene isomers were found in this experiment at expected retention times. By comparison to Fig. S65(b), the signal ratios seem to corresponds to a medium to large applied potential in the ¹²C experiment. Furthermore, the lack of any signal within the reference experiment on carbon paper confirms eCO2R on copper as butene origin.

As no $C_4H_9^+$ signal is seen in Fig. S65(a), butadiene was not observed in the ¹³C experiment. This is most likely caused by the relatively large current at which butadiene selectivity is very small. As mentioned above, the butene production seems to be corresponding to a medium to large applied potential at which butadiene production was



S65(a): XIC of relevant traces indicating C_4 hydrocarbons within ¹³C experiment.

S65(b): XIC of $C_4H_9^+$ signals observed across different ¹²C experiments.

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Figure S65: Verification of butene production through reference experiment analysis.

hardly observable in the ¹²C experiment, see appendix D.9. Yet, it has been observed consistently within four independent measurements and the flat baseline signals of reference experiments in Fig. S66 confirm these are not artefacts or systematic errors.



Figure S66: *XIC of* $C_4H_7^+$ *signals observed across different* ¹²C *experiments.*

F.4.2 Acetone, propanal, and allyl alcohol

For verification of the different C_3H_6O isomers reported in appendix D.11, corresponding secondary ions detected in the ¹³C experiment are shown in Fig. S67(a). All three reported isomers were also found in this experiment, the acetone signal is expectedly small in

comparison with propanal and allyl alcohol.



S67(a): XIC of relevant traces indicating C_3H_6O isomers within ¹³C experiment, including indicators of their retention times.



S67(b): XIC of $C_3H_5^+$ across different ¹²C experiments, including indicators of C_3H_6O isomers' retention timeframes.

Figure S67: Verification of C₃H₆O isomers production through reference experiment *analysis.*

As expected, propanal peak includes $C_3H_5^+$, $C_3H_9O^+$, and $C_3H_3^+$. Acetone peak includes $C_3H_5^+$. Allyl alcohol peak includes $C_3H_5^+$ and $C_3H_3^+$. The eCO2R origin of these products could be confirmed by the reference experiment as no corresponding peaks were registered beyond the baseline signal, see Fig. S67(b).

F.4.3 Pentene and propanol

To confirm the observed pentene signal overlapping with propanol signal discussed in appendix D.12, corresponding secondary ions detected in the ¹³C experiment are shown in Fig. S68(a). The relative signals show a peak of $C_5H_{11}^+$ a few seconds before the propanol-related C_3 traces are peaking as indicated by the thick black dashed lines. As 1-pentene production is not very large even at this applied potential, the absolute intensities are much smaller than for propanol, the suspicion of $C_3H_3^+$ as partially originating from pentene can therefore not be confirmed. What can be observed though are two additional peaks in the minute after 1-pentene elution that might indicate additional isomers - most likely 2-pentene stereoisomers analogous to butene observations in appendix D.9. These are indicated by thin gray dashed lines.

The additional peaks found correspond well with those observed in the ¹²C experiments at some of the applied potentials as shown in Fig. S68(b): the second peak appears ≈ 10 s and the third ≈ 50 s after the initial one. The flat baseline signal of the reference experiment on carbon paper confirms eCO2R on copper as product origin.



S68(a): XIC of relevant traces indicating pentene and/or propanol within ¹³C experiment, including indicators of their retention times.



S68(b): Relative signal of $C_5H_{11}^+$ across different ¹²C experiments, including indicators of pentene's suspected retention timeframes.

Figure S68: Verification of pentene production through reference experiment analysis.

F.4.4 Butanedione

Butanedione was confirmed in the ${}^{13}C$ experiment as shown in Fig. S69(a).



S69(a): XIC of relevant traces indicating butanedione within 13 C experiment.



S69(b): XIC of $C_4H_7O_2^+$ across different ¹²C experiments.

Figure S69: Verification of butanedione through reference experiment analysis.

Both secondary ions reported in appendix D.13 were observed and even an isotope of the main ion response, ${}^{13}C^{12}CH_3O^+$, which based on the small ${}^{12}C$ impurities of the CO₂ used, was identified. The flat baseline signal of the reference experiment on carbon paper

shown in Fig. S69 confirms eCO2R on copper as product origin.

F.4.5 Butanal and butanone

For verification of the two C_4H_8O isomers reported in appendix D.14, corresponding secondary ions detected in the ¹³C experiment are shown in Fig. S70(a). The shift between peaks of $C_4H_9O^+$ and $C_4H_7^+$ trace of ≈ 15 s was observed again, confirming the suspicion of separate butanal and butanone identification analogous to C_3H_6O isomers.



S70(a): XIC of relevant traces indicating C_4H_8O isomers within ¹³C experiment, including indicators of their retention times.



S70(b): XIC of $C_4H_9O^+$ across different ¹²C experiments.

Figure S70: Verification of C₃H₆O isomers production through reference experiment *analysis.*

The substantially larger peak of $C_4H_9O^+$ shown in Fig. S70(b) does not allow for discrimination between the two species that has been established with the help of a butanone standard as mentioned in appendix D.14. The flat baseline signal of the reference experiment on carbon paper confirms eCO2R on copper as product origin.

F.4.6 Ethyl acetate

Ethyl acetate was confirmed in the ¹³C experiment as shown in Fig. S71(a). The three main ion responses reported in appendix D.13 were observed at the expected retention time. The flat baseline signal of the reference experiment on carbon paper shown in Fig. S71(b) confirms eCO2R on copper as product origin.



S71(a): XIC of relevant traces indicating ethyl acetate within 13 C experiment.

S71(b): XIC of $C_4H_9O_2^+$ across different ¹²C experiments.

Figure S71: Verification of ethyl acetate production via reference experiment analysis.

F.4.7 Pentanedione isomers

For verification of the pentanedione isomers reported in appendix D.16, corresponding secondary ions detected in the 13 C experiment are shown in Fig. S72(a).



S72(a): XIC of relevant traces indicating pentanedione within ¹³C experiment, including indicators of their retention times.



S72(b): XIC of $C_5H_9O_2^+$ signals observed across different ${}^{12}C$ experiments.

Figure S72: Verification of pentanedione production via reference experiment analysis.

Both secondary ions reported in appendix D.16 were observed and even an isotope of the main ion response, ${}^{13}C^{12}CH_3O^+$, which based on the small ${}^{12}C$ impurities of the CO₂

used, was identified. For these ions, both peaks corresponding to the different isomers were found in this experiment at expected retention times: a smaller first one and a much larger second one ≈ 140 s later. The flat baseline signal of the reference experiments shown in Fig. S72(b) confirm eCO2R on copper as product origin.

G Quantifiaction of abundance

Absolute quantification of species concentrations is not possible within acceptable errors due to a number of factors: First of all, RRCs are only reported for SIFT-MS. Even if these can be adopted unaltered for PTR-MS, high species abundance will cause them to not be consant anymore as discussed in appendix E.2. Furthermore, we only analyse the gas outlet, liquid products are therefore only present based on their vapour-liquid-equilibrium (VLE). To compensate for this effect, Henry's law can be used - but it is technicallz only applicable for infinite dilution and values are only available for binary systems with water. Lastly, volume fluxes needed for determination of absolute concentrations are ambiguous, therefore the PTR-MS would have to be calibrated for each identified product individually.

We still can try to correct for RRC and VLE with the values that are available and compare orders of magnitude expected for absolute Faradaic Efficiencies. A corrected and compensated signal as indirect measure for absolute yield can be calculated via

$$c_{r,i}\left(\mathbf{U}_{\mathrm{Hg/HgO}}\right) = \int_{j} I_{3}\left(\mathbf{U}_{\mathrm{Hg/HgO}}\right) / k_{c} / x_{\mathrm{PI}} \times H^{cp} / J_{\mathrm{total}} \times n_{\mathrm{e}^{-}}, \qquad (G.1)$$

where $\int_{j} I_3 (U_{Hg/HgO})$ is the sum of all integrated signals originating from the same primary ion ionizing a species. The fraction of the primary ion used is given by x_{PI} and the number of electrons transferred to form the product in question. The constant of Henry's law for mixtures with water is given by H^{cp} but only applied in Eq. (G.1) for liuid products under the given conditions.

The parameters needed for correcting and compensating signals as well as the final values are given in Tab. S37. Reaction rate coefficients are taken from SIFT publications given in appendix E.1.2. If the value is orange, no value was available and is therefore estimated. Henry's law constants for water as solvent from [26].

Furthermore, some secondary ions could not be unambiguously assigned to a primary ion, creating uncertainties. The primary ions for the corresponding species are given in orange. Lastly, total signal could not be assigned confidently to a handful of species as they showed significant overlap with another species. The total signal strength as well as compensated values are therefore highlighted yellow. As expected, the absolute quantification is not very precise, especially when O_2^+ and H_3O^+ values differ a lot and for liquid products. Closer examination shows that correction via Henry coefficients is flawed: for example, comparing ethanol with 2,3-pentanedione at $U_{Hg/HgO} = 2.0 V$ or acetaldehyde with acetone and 2,4-pentanedione at $U_{Hg/HgO} = 3.5 \text{ V}$ shows an obvious mismatch of corrected values between products of smaller and larger boiling points. It becomes clear that the underlying assumption of using Henry's law - namely, concentration of products with high boiling points detected in the liquid phase being in equilibrium with the electrolyte as the liquid phase - is not remotely applicable. In fact, most of these products seem to enter the gaseous phase - diffusing to the gas channel - directly, with only a small fraction finding its way into the electrolyte permanently. This suspicion is confirmed by NMR analysis of the catholyte documented in section H. Comparison of gaseous products, on the other hand, at least seems to be correct in orders of magnitude.

	product			Primary Ion			uns	a of raw integra	ted signals Σ_{i} .	J _j I ₃ (U _{Hg/HgO}				con	rected and com	pensated signal	ls c _{r,i} (U _{Hg/HgO}		
name	n_{e^-}	$H^{cp}\left[\frac{\text{mol}}{\text{m}^3 \text{ Pa}}\right]$	type k	$c \left[\frac{10^{-9} \text{cm}^3}{\text{s}} \right]$	purity	2000 mV	2500 mV	3000 m V	3500 mV	4000 mV	4500 mV	5000mV	2000 mV	2500 mV	3000 mV	3500mV	4000 mV	4500 mV	5000 mV
carbon monoxide	2	$9.70 imes 10^{-6}$	H_3O^+	0.001	97.56%	$2.5 imes 10^2$	$3.2 imes 10^2$	$2.2 imes 10^2$	$1.8 imes 10^2$	$1.8 imes 10^2$	0.0	0.0	$2.7 imes 10^6$	$1.6 imes 10^6$	8.4×10^{5}	4.8×10^5	$4.0 imes 10^5$	0.0	0.0
methane	~	1.40×10^{-5}	$0^{2^{+}}$	0.005	1.95%	0.0	0.0	2.5×10^{3}	5.6×10^{3}	1.1×10^{4}	1.1×10^{4}	1.2×10^{4}	0.0	0.0	3.7×10^{8}	6.1×10^{8}	1.0×10^{9}	8.7×10^8	6.2×10^{8}
ethylene	12	$5.90 imes 10^{-5}$	$^{\rm H_3O^+}_{ m O^2^+}$	0.063 1	97.56% 1.95%	2.5×10^{5} 6.1×10^{3}	1.3×10^{6} 1.1×10^{4}	1.7×10^{6} 1.1×10^{4}	1.9×10^{6} 1.1×10^{4}	7.3×10^{5} 9.4×10^{3}	4.1×10^{5} 7.3×10^{3}	6.2×10^{5} 8.6×10^{3}	2.6×10^8 2.0×10^7	6.1×10^{8} 1.7×10^{7}	6.0×10^{8} 1.3×10^{7}	4.9×10^{8} 8.8×10^{6}	1.6×10^{8} 6.4×10^{6}	7.6×10^{7} 4.2×10^{6}	7.3×10^7 3.2×10^6
formaldehyde	4	3.20×10^{1}	H ₃ O ⁺	3.4	97.56%	2.1×10^{4}	2.0×10^4	2.6×10^{4}	3.1×10^{4}	3.5×10^4	3.3×10^{4}	3.9×10^{4}	4.3×10^{6}	1.9×10^{6}	1.9×10^{6}	1.6×10^{6}	1.5×10^{6}	1.2×10^{6}	9.2×10^{5}
methanol	9	2.20	H_3O^+	2.7	97.56%	3.7×10^{3}	3.5×10^3	4.0×10^{3}	4.0×10^{3}	4.2×10^{3}	4.4×10^{3}	4.7×10^{3}	9.8×10^{4}	4.2×10^{4}	3.7×10^{4}	2.6×10^4	2.3×10^4	2.1×10^{4}	1.4×10^{4}
propylene	18	4.70×10^{-5}	$^{ m O2^+}_{ m H_3O^+}$	1.5 1.3	1.95% 97.56%	2.3×10^2 5.5×10^5	6.8×10^{2} 1.8×10^{6}	6.6×10^{2} 1.7×10^{6}	9.2×10^{2} 1.7×10^{6}	3.0×10^{2} 4.3×10^{5}	2.2×10^2 2.6×10^5	1.6×10^{2} 3.1×10^{5}	7.4×10^{5} 4.2×10^{7}	1.0×10^{6} 6.3×10^{7}	7.5×10^5 4.5×10^7	7.4×10^5 3.1×10^7	2.1×10^{5} 6.8×10^{6}	1.3×10^{5} 3.5×10^{6}	5.8×10^{4} 2.6×10^{6}
acetaldehyde	10	$1.30 imes 10^{-1}$	H ³ O ⁺	3.7	97.56% 1 95%	6.0×10^{5} 6.2×10^{2}	2.2×10^{6} 1.6 $\times 10^{3}$	2.1×10^{6} 2.7×10^{3}	2.0×10^{6} 3.7×10^{3}	2.0×10^{6} 3.2×10^{3}	2.2×10^{6} 2.6×10^{3}	2.0×10^{6} 1 8 \lapla 10 ³	8.7×10^{6} 5.4 \sim 10^{5}	1.5×10^7 6.6 \laperturbed{10^5}	1.1×10^7 8 3 $\times 10^5$	7.5×10^{6} 6 9 \lapha 10^{5}	6.2×10^{6} 5 8 $\times 10^{5}$	5.7×10^{6} 4.0×10^{5}	3.4×10^{6} 1 8 \circ 10^{5}
	5	00 -	H ₃ 0 ⁺	2.7	97.56%	1.9×10^{5}	1.0×10^{5} 2.3 × 10^{5}	$\frac{2.1 \times 10}{4.4 \times 10^{5}}$	7.8×10^{5}	$\frac{3.2 \times 10}{1.4 \times 10^6}$	$\frac{2.0 \times 10}{1.6 \times 10^6}$	1.6×10^{6}	8.9×10^{6}	4.8×10^{6}	7.0×10^{6}	0.9×10^{6} 8.9 × 10 ⁶	1.3×10^7	$\frac{4.0 \times 10}{1.3 \times 10^7}$	8.5×10^{6}
ethanol	17	1.90	02+0	2.3	1.95%	3.9×10^{3}	$5.2 imes 10^3$	8.9×10^{3}	1.1×10^{4}	1.3×10^{4}	1.3×10^{4}	1.0×10^{4}	1.1×10^{7}	6.4×10^{6}	8.4×10^{6}	7.5×10^{6}	7.5×10^{6}	6.3×10^{6}	3.2×10^{6}
1-butene	24	3.90×10^{-5}	$H_{3}O^{+}$	1.6	97.56%	6.6×10^{2}	$5.6 imes 10^2$	9.3×10^2	1.6×10^{3}	1.9×10^{3}	3.7×10^3	5.5×10^3	5.4×10^{4}	2.1×10^4	2.7×10^4	3.3×10^4	3.2×10^4	5.4×10^{4}	5.1×10^4
butadiene	22	1.00×10^{-4}	H_3O^+	1.6	97.56%	2.9×10^2	1.9×10^{3}	7.4×10^{2}	4.5×10^{2}	9.8×10^{1}	1.4×10^{2}	7.3×10^{1}	2.1×10^{4}	6.3×10^{4}	1.9×10^{4}	8.3×10^{3}	1.5×10^3	1.9×10^{3}	6.3×10^{2}
trans-2-	24	$5.00 imes 10^{-5}$	H ₃ O ⁺	1.6	97.56%	2.0×10^{3}	2.1×10^{3}	1.5×10^3	8.4×10^{2}	5.8×10^2	4.0×10^{2}	3.9×10^{2}	1.6×10^{5}	8.0×10^4	4.3×10^{4}	1.7×10^{4}	9.9×10^{3}	5.8×10^3	3.6×10^{3}
butene						c.	5		c.	c,	0	c.							c,
cis-2- butene	24	5.00×10^{-3}	H30 ⁺	1.6	97.56%	5.6×10^{2}	3.1×10^{2}	2.6×10^{3}	1.6×10^{2}	7.4×10^{2}	6.0×10^{2}	9.1×10^{2}	4.5×10^4	1.2×10^{2}	7.4×10^{4}	3.3×10^{4}	1.3×10^{4}	8.8×10^{2}	8.5×10^{2}
cyclopropane	18	1.10×10^{-4}	02+	1.3	1.95%	2.3×10^2	$5.9 imes 10^2$	3.1×10^2	2.6×10^2	3.4×10^{2}	1.3×10^{2}	3.1×10^{2}	8.5×10^{5}	1.0×10^{6}	4.0×10^{5}	2.5×10^5	2.7×10^{5}	8.9×10^{4}	1.3×10^{5}
propanal	16	9.90×10^{-2}	H_3O^+	3.6	97.56%	5.5×10^{5}	1.7×10^{6}	1.6×10^{6}	1.4×10^{6}	6.3×10^{5}	3.2×10^{5}	1.9×10^{5}	1.3×10^7	1.8×10^7	1.3×10^7	8.1×10^{6}	3.2×10^{6}	1.4×10^{6}	5.3×10^{5}
acetone	16	2.70×10^{-1}	$H_{3}O^{+}$	3.9	97.56%	1.8×10^{3}	$6.5 imes 10^2$	1.6×10^3	$3.2 imes 10^3$	$5.0 imes 10^3$	4.9×10^3	5.2×10^{3}	4.1×10^{4}	6.6×10^3	1.3×10^{4}	1.7×10^{4}	2.3×10^4	1.9×10^{4}	1.3×10^{4}
allyl alcohol	16	2.00	H ₃ O ⁺	2	97.56%	7.9×10^{3}	9.0×10^3	1.4×10^{4}	2.4×10^{4}	$3.5 imes 10^4$	4.0×10^4	3.8×10^{4}	6.9×10^{5}	3.6×10^{5}	4.4×10^{5}	$5.1 imes 10^5$	6.3×10^{5}	6.3×10^{5}	3.7×10^5
pentene	30	2.50×10^{-5}	H_3O^+	1.9	97.56%	6.2×10^{2}	4.5×10^{2}	2.0×10^3	3.5×10^3	3.3×10^{3}	3.1×10^{3}	3.4×10^{3}	5.3×10^{4}	1.8×10^{4}	6.0×10^{4}	7.4×10^{4}	5.9×10^4	4.8×10^{4}	3.3×10^{4}
propanol	18	1.40	H_3O^+	2.7	97.56%	9.6×10^{4}	2.1×10^{5}	5.8×10^{5}	8.7×10^{5}	1.0×10^{6}	8.2×10^{5}	7.3×10^{5}	4.9×10^{6}	5.0×10^{6}	1.0×10^{7}	1.1×10^7	1.1×10^{7}	7.5×10^{6}	4.2×10^{6}
butanedione	18	7.30×10^{-1}	$H_{3}O^{+}$	1.7	97.56%	4.0×10^{3}	7.4×10^{4}	3.4×10^{5}	6.1×10^{5}	9.7×10^{5}	5.4×10^{5}	2.6×10^{5}	2.3×10^{5}	1.9×10^{6}	6.8×10^{6}	8.7×10^{6}	1.2×10^7	5.6×10^{6}	1.7×10^{6}
butanone	22	2.00×10^{-1}	H_3O^+	3.9	97.56%	8.6×10^3	3.1×10^{4}	5.9×10^{4}	9.2×10^4	7.6×10^4	4.8×10^4	2.6×10^4	2.6×10^5	4.4×10^5	6.3×10^5	7.0×10^{5}	4.8×10^5	2.6×10^5	8.9×10^4
butanal	22	9.50×10^{-2}	H_3O^+	3.8	97.56%	7.9×10^{2}	4.2×10^{3}	4.2×10^{3}	2.5×10^3	1.6×10^{3}	7.8×10^{2}	5.9×10^{2}	2.5×10^4	6.0×10^{4}	4.6×10^{4}	1.9×10^{4}	1.0×10^{4}	4.4×10^{3}	2.1×10^{3}
ethyl acetate	20	$5.90 imes 10^{-2}$	H ₃ O ⁺	2.9	97.56%	4.6×10^{3}	1.0×10^{4}	3.2×10^{4}	6.9×10^4	8.7×10^4	$5.7 imes 10^4$	3.2×10^{4}	1.7×10^{5}	1.7×10^{5}	4.2×10^{5}	6.4×10^{5}	6.7×10^{5}	3.8×10^{5}	1.4×10^{5}
2,3-pentane- dione	30	3.77×10^{1}	H ₃ O ⁺	1.88	97.56%	3.7×10^3	9.0×10^3	$5.1 imes 10^3$	3.0×10^{3}	2.4×10^{3}	0.0	0.0	1.2×10^7	1.3×10^7	5.8×10^{6}	2.4×10^{6}	1.7×10^{6}	0.0	0.0
2,4-pentane- dione	30	4.30	H ₃ 0 ⁺	1.88	97.56%	1.0×10^{4}	$6.5 imes 10^4$	9.8×10^{4}	8.8×10^{4}	3.0×10^{4}	1.4×10^{4}	8.0×10^{3}	3.8×10^{6}	1.1×10^{7}	1.3×10^{7}	8.1×10^{6}	2.3×10^{6}	9.5×10^{5}	3.4×10^{5}

 Table S37: Total signal strength for each product and compensation for VLE as well as RRC.

A second way to attain more absolute quantitative information on eCO2R yields is to analyse the signal of remaining CO_2 at the GDE outlet. Within the original measurements, CO_2 was observed at its expected retention time through ionization of residual O_2^+ , see section D.3. We observe slightly decreasing signal strengths for all applied potentials, indicating increased CO_2 consumption as expected. Due to possible dilution by hydrogen (via competing HER), quantification is again not possible.

As shown in Fig. S73, a comparison with non-reacting carbon dioxide, as observed in the reference experiment with carbon paper instead of a copper catalyst as described in section F.1, is possible though. Since HER is the only reaction driving the large current here, dilution via hydrogen is at a maximum. Nonetheless, CO₂ signals are at $\approx 150\%$ of the eCO2R measurements, considering peak areas.



Figure S73: *XIC for* CO_2^+ *ion from different experiments.*

H NMR catholyte analysis

H.1 Methodology

H.1.1 Experimental procedure

NMR spectra were recorded using Magritek Spinsolve 60MHz bench-top spectrometer. The measurement was cariied out with the following procedure: 10mL catholyte sample were extracted after 20min of electrochemical reaction. 10μ L of a 1-molar dimethyl-sulfoxide (DMSO) solution was added as a standard, then the ¹H NMR spectrum was recorded. Solvent suppression mode (Spinsolve ULTRA) was used in order to minimize the water signal.

H.1.2 Data processing and analysis

Spectra were generated by Fourier Transformation of raw data and subsequent filtering via moving average. The DMSO peak was easily identified its known chemical shift of 2.6 ppm used as reference point for all other species. These were identified by their known chemical shifts listed in Tab. S38. The full spectra in Fig. S74 shows that a few products are readily identifable due to distinctive peak levels and types: formate, acetate, and ethanol (signals related to both groups).



Figure S74: ¹H NMR spectrum on a sample of catholyte including DMSO standard.

Comparing the chemical shifts in our experiment to the literature, we found general deviation of about -0.13 ppm compared to SDBSWeb data [27] and on average -0.03 ppm compared to Kuhl et al.[7] who undertook similar measurements with catholyte of eCO2R experiment. Expected chemical shifts of all other possible products were therefore calculated based on these trends and shown in Tab. S38.

 Table S38: Reference data used for data analysis: literature data of peak types and known chemical shifts related to expected species.

spec	cies derived from	peak	MHz	solv.	SDBSWeb [27] signal fraction	ppm	Kuhl [7] ppm	other source ppm	expected ppm
Formaldehyde Methanediol	formaldehyde	s s	300	TMS	1000	9.60 -		9.60 [28] (DMSO) 4.84 [29]	
Methanol		s	600	H2O	100	3.34	3.23		3.21
Acetaldehyde		d	300	CDC13	1000/1000	2.21	2.12		2.08
,		q			250/90/250/90	9.79	9.55	1 11 [20]	9.66
1,1-Ethanediol	Acetaldehyde	d q	-	-			5.13	1.11 [30]	5.06
Ethanol		t q	600	H2O	50/100/50 16/47/47/16	1.17 3.65	1.06 3.53		1.04 3.51
		t			60/100/60	1.04	0.92		0.91
Propanal		m	600	H2O	10/10/20/20/10	2.55	2.44 (q)		2.42
		t			9/13/9	9.69	9.57 (s)	0.72 [20]	9.56
1.1.Propagadiol	Propagal	L m					0.78	1.4 [30]	0.73
1,1-1 Topanedior	Tiopanai	t					4.85	4.76 [30]	4.80
Acetone		s	500	H2O	100	2.22	2.10		2.08
		d					5.07		5.05
Allyl alcohol		d					5.17		5.15
		m					5.90		5.88
		dt t			50/100/50	0.88	3.99		3.97
Propanol		m	500	H2O	5/20/40/40/20/5	1.54	1.42		1.41
		t			45/85/45	3.55	3.44		3.42
Butanedione		s	300	CDCl3	1000	2.34			2.21
		t			30/55/30	1.06			0.93
Butanone		s	500	CDCl3	100	2.14			2.01
		q			9/26/26/9	2.46			2.33
		l n			50/100/30	1.61			1.48
Butanal		m	600	H2O	17/17/31/31/17/17	2.50			2.37
		t			16/9/9	9.66			9.53
		t			215/560/245	1.26			1.13
Ethyl Acetate		s	90	CDCl3	1000	2.04			1.91
		<u>q</u>			60/180/180/60	4.12			3.99
2 3-Pentanedione		s i	90	CDC13	1000	2.34			2.21
2,0 1 011110010110		q	10	02013	70/170/150/50	2.77			2.64
Formic Acid		s	500	H2O	100	8.44	8.33		8.31
Acetic Acid		s	500	H2O	100	1.91	1.87		1.78
Propionic Acid		t	500	H2O	50/100/50	1.04			0.91
		q			20/50/50/20	2.17			2.04
		d			100/50	0.32 6.36			6.19
Acrolein		m			40/600/300/300/300/400	6.51			6.38
		d			500/500	9.59			9.46
Glyoxal Glycolic Acid	Glyoxal	d s	500	H2O	100	3.94			3.81
Church Halten	,	d			300000/300000	3.50			3.37
Glycolaldehyde		t		D2O	80000/150000/70000	5.05			4.92
		s			9000	9.62			9.49
1,1,2-Ethanetriol	Glycolaldehyde	d					3.40		3.38
Ethylana glucal	,, ,	t	400	CDCl2	100/50/1000/500/50	2 71	4.94		4.92
Euryrene grycol		- III - e	400	CDCIS	100/30/1000/300/30	2.17	2.02		2.02
Hydroxyacetone		s	90	CDCl3	350	3.26	2.02		3.13
		s			600	4.26	4.25		4.13
DMSO		s	300	CDCl3	1000	2.62	2.60		2.60

H.2 Species identification

The fact that not many different products are observed confirms our suspicion that only very small amounts of even those products with comparatively high boiling points stay in the liquid phase, see also section G. This confirms our focus on product identification at the gas outlet as a practical way to derive information on the active rection mechanism in high-current GDEs. Furthermore, we can confirm that no major signals of formerly undetected products, except for formic acid and acetic acid which have been observed in a previous study as well [31]. Especially the lack of other double-oxygenated products confirms the related hypotheses mentioned in the manuscript.



S75(a): Zoomed extract of NMR spectrum in the vicinity of water peak.



S75(b): Zoomed extract of NMR spectrum in the vicinity of zero chemical shift.

Figure S75: ¹H *NMR spectrum on a sample of catholyte including DMSO standard including indicators of observed products.*

Fig. S75 shows interesting extracts of the spectrum including species discussed below. While no other very pronounced peaks are visible at first glance, a few more significant data points can be seen and moreover are both ethanol signals quite asymmetric and warrant further investigation. We approach this systematically by functional groups, products found are marked bold.

H.2.1 Carboxylic acids

Carboxylic acids could not be found via PTR-MS as they were deprotonated due to the alkaline conditions and therefore did not enter the gas phase. As expected, some carboxy-lates were found in the electrolyte though:

- Formate: The singlet at 8.31 ppm is very pronounced as shown in Fig. S74.
- Acetate: The singlet at 1.78 ppm is quite pronounced although smaller than formate signal as shown in Fig. S74.
- Propionic Acid: Triplet at 0.91 ppm coincides with ethanol but the quartet at 2.17 ppm should be well visible in Fig. S75(a). We conclude that no substantial quantities are produced.

H.2.2 Alcohols

Primary alcohols are the second category of products that can be clearly observed as they do not form hydrates and are sensitive to ¹H NMR.

- Methanol: Even though some traces are observed in the gas phase (see section D.5, the singlet at 3.21 ppm is not observable in Fig. S75(a).
- Ethanol: Large signals were observed with PTR-MS (see section D.8), and here as well:
 - The triplet at 1.04 ppm is quite strong. On closer examination it seems that that signals do not exactly follow the expected 1:2:1 pattern (i.e. 25%: 50%: 25%). Calculated peak ares give 30%: 42%: 27%, which indicates that another signal might overlap on the left side of the triplet in Fig. S75(a).
 - The quartet at 3.51 ppm is also quite strong, yet signals are expectedly a bit weaker than for the triplet. On closer examination it seems that that signals do not exactly follow the expected 1:3:3:1 pattern (i.e. 13% : 37% : 37% : 13%). Calculated peak ares give 12% : 33% : 38% : 17%, which indicates that another signal might overlap on the right side of the quartet in Fig. \$75(b).
- **Propanol:** Substantial signals were observed with PTR-MS (see section D.12); on closer examination, we also find some evidence here: While the first triplet expected at 0.75 ppm and sextet expected at 1.41 ppm are not clearly pronounced (yet some signal is detected amongst the noise in Fig. S75(a)), we find some evidence for the second triplet at 3.42 ppm (see Fig. S75(b). This coincides with the right side of the ethanol quartet and explains its skewed signal pattern mentioned above.

H.2.3 Aldehydes

Aldehydes are somewhat harder to detect as they can be hydrated to diols in aqueous solutions which is sometimes even the more stable structure under our experimental conditons [7].

- Formaldehyde: This is observed in the gas phase with PTR-MS, see section D.5. The corresponding singlet at 3.21 ppm is not observed in Fig. S75(b).
- Acetaldehyde: The corresponding doublet and quartet expected at 2.08 ppm and 9.66 ppm could not be observed which is expected as the hydrated form ethanediol is preferred. Unfortunately, ethanediol's corresponding quartet expected at 5.13 ppm coincides with the large water signal, but we find some evidence for the doublet at 1.14 ppm (see Fig. S75(a). This coincides with the left side of the ethanol triplet and explains its skewed signal pattern mentioned above.
- **Propanal:** Corresponding triplets at 0.91 ppm and 9.56 ppm could not be verified which is expected as the hydrated form propanediol is preferred. Unfortunately, propanediol's first triplet expected at 4.80 ppm coincides with the large water signal, but the second triplet at 0.73 ppm was observed.

H.2.4 Others

- Ketones were not observed, just a few small indicators of potentially corresponding singlets around ≈ 2.10 ppm were found.
- *Diones* were possibly detected, signal-to-noise ratio is too small to confirm this though. The elevated signals around ≈ 2.10 ppm might also correspond to the singlets of butanedione and pentanedione.
- Double-oxygenated $C_2 C_3$ species were not detected: Glyoxal's hydrated form glycolic acid would show a singlet around 3.81 ppm in Fig. S75(b). Neither were any signals corresponding to hydroxyacetone and glycolaldehyde (or its hydrated form) detected.

I Kinetic Isotope Effect

I.1 Calculation of shift

Usually the shift is calculated as follows:

$$\delta^{13} \mathcal{C}(\%) = \left[\frac{\begin{pmatrix} \frac{13}{6} \mathcal{C} \\ \frac{6}{6} \mathcal{C} \end{pmatrix}}{\begin{pmatrix} \frac{13}{6} \mathcal{C} \\ \frac{6}{6} \mathcal{C} \end{pmatrix}}_{\mathrm{CO}_2} \right] \times 1000 \,\mathrm{where} \, \left(\frac{13}{6} \mathcal{C} \\ \frac{12}{6} \mathcal{C} \right)_{\mathrm{sample}} = \frac{I \begin{pmatrix} 13 \\ 6 \mathcal{C} \end{pmatrix}_{\mathrm{species}}}{I \begin{pmatrix} 12 \\ 6 \mathcal{C} \end{pmatrix}_{\mathrm{species}} \times n \, (\mathcal{C})_{\mathrm{species}}} \quad (\mathrm{I.1})$$

This yields the more fundamental version of

$$\delta^{13} \mathbf{C} (\%) = \left[\frac{\frac{I(\frac{13}{6}\mathbf{C})_{\text{sample}}}{I(\frac{12}{6}\mathbf{C})_{\text{sample}} \times n(\mathbf{C})_{\text{sample}}}}{\frac{I(\frac{13}{6}\mathbf{C})_{\text{co}_2}}{I(\frac{13}{6}\mathbf{C})_{\text{co}_2} \times n(\mathbf{C})_{\text{co}_2}}} - 1 \right] \times 1000$$
(I.2)

We can see that this is only a specific case of the more widely applicable

$$\delta^{13}C(\%) = \begin{bmatrix} \frac{I(\frac{i_{0}^{12}C_{x}, \frac{i_{0}^{2}C_{n-x}}{sample}}{I(\frac{i_{0}^{12}C_{0}}{I(\frac{i_{0}^{2}C_{0}}{2})} \times \binom{n}{x}}{-1} \end{bmatrix} \times 1000 \quad \text{with} \quad n = n(C)_{\text{species}} \quad (I.3)$$

The commonly used version in Eq. I.1 is therefore only a more specific version of Eq. I.3 x = 1 which makes sense since most of the time only the single-isotope version is found. For larger hydrocarbon chains multi-isotope versions become more probable though and can be used to verify the ¹³C shift and distinguish traces.

For an intermediate or product $(H_xC_yO_z^+ \text{ at a given } m/z)$, its isotope peak (m/z + 1.003) not only contains ${}^{1}H_x {}^{12}C_{y-1} {}^{16}O_z {}^{13}C^+$ but also other isotopologues, such as ${}^{1}H_{x-1} {}^{12}C_y {}^{16}O_z {}^{2}H^+$ and ${}^{1}H_x {}^{12}C_y {}^{16}O_{z-1} {}^{18}O^+$, due to the isotopic natural abundance in reactants. Therefore, a small correction for this effect is necessary and is performed in the present work using IsoCor v2 (implemented in Python 3) [32].

Choice of ion can skew the calculated shift if we choose a fragment or cluster where a carbon was added or removed form the original secondary ion. This can happen for two reasons:

- 1. Increased selectivity towards ¹²C over ¹³C in CO2R specific to asymmetrical steps. This means that the carbon atoms have different probabilities to be one isotope or the other. For this reason, after dissociation of a carbon-containing species (which is specific to the carbon depending on its structure), the δ ¹³C will be different than before.
- 2. The fragmentation or clustering reaction in the drift tube itself discriminates between carbon isotopes.

I.2 Individual species

Recently, the tracking of ¹³C isotopes of protonated analyte has been suggested as a means for CO2R product analysis. [31] Analogous to other carbon-conversion processes, a kinetic isotope effect can be observed as the ratio of ¹³C isotopes drops below levels of natural abundance due to increased selectivity for ¹²C isotopes as reactant. Wherever possible, we calculated δ^{13} C as a measure for this shift of isotope ratios.

For most of the products detected this was not possible with sufficient accuracy as the system was designed rather for species identification than very accurate signal quantification. Especially the low dilution level leads to such high concentrations for the most abundant species that effects described in section E.2 take effect and skew results. On the other hand, most less-abundant species are still observed at concentrations too small for accurate determination of the effect as ¹³C isotope traces are observed only with very small signal-to-noise ratios. The only products for which the Kinetic Isotope Effect could be calculated and discussed with sufficient confidence are the C₃ species propylene, propanol, and propanal shown in Fig. S76.



Figure S76: *Kinetic Isotope Effect of selected traces representing* C₃ *products across the range of applied potential.*

The initial value at $J \approx 200 \,\mathrm{A\,cm^{-2}}$ for propanal is similar to the benchmark [31] as is the trend towards bigger shifts with larger currents - including the indicated inflection point towards slightly smaller shifts again around $J \approx 500 \,\mathrm{A\,cm^{-2}}$. For propanol and propylene, initial values deviate a lot from the benchmark but their average is close to the reported value (as the two are not distinguished in [31]). The trend of propanol for bigger shifts with larger currents corresponds to the initial trend reported and the trend of propylene towards smaller shifts corresponds to the later trend around $J > 400 \,\mathrm{A\,cm^{-2}}$. A noteworthy observation is that the alcohol shows a smaller shift towards ¹²C than the alkene for smaller currents, but this gets inverted at a medium current density due to increasing shift for the alcohol and decreasing shift for the alkene.

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