Electronic Supplementary Material (ESI) for Dalton Transactions.

Manifesto for the routine use of NMR for the liquid product analysis of aqueous CO_2 reduction: from comprehensive chemical shift data to formaldehyde quantification in water

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Supporting Information

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S1 – Material and solvents

Following compounds are purchased from the mentioned suppliers:

Sigma-Aldrich : Deuterium oxide (D_2O), Dimethyl sulfoxide 99.8% (DMSO), and Dimethyl sulfone NMR standard grade ($DMSO_2$), 3-(Trimethylsilyl)propane-1-sulfonate sodium salt (DSS), Methanol, Formaldehyde (37% in water, stabilized with 15-20% methanol), Sodium bisulfite ACS Reagent, Lactaldehyde, DL-Glyceraldehyde, β-Hydroxypyruvic acid, Sodium mesoxalate monohydrate, Acrolein, Glycerol, Propionic acid, Malonic acid, Propargyl alcohol, Methyl acetate, 2-Hydroxyethyl formate, Potassium formate, Acetaldehyde, Glyoxal 40 wt % in H_2O, Acetic acid, glyoxylic acid, Glycolic acid, Isopropanol. **Alfa Aesar:** Pyruvic acid, Propan-1-ol, 1,2-Propanediol, 1,3-Propanediol, Pyruvic aldehyde (35-45% w/w aq. Soln), Lactic acid, Hydroxyacetone, Pyruvic acid, Glyceric acid, Dihydroxyacetone, Tartronic acid, Allyl alcohol, Acrylic acid, 2-Methoxyacetic acid, Methyl glycolate, 1,3,5-Trioxane. **TCI Chemical:** 2-Methoxyethanol, Dimethyl Carbonate, Dimethoxymethane, Ethylene glycol, Methyl formate. **ACROS Organics:** Pyruvic acid. **VWR Chemicals:** Acetone. **Merck:** Ethanol.

Materials were used as received. milliQ water (resistance 18.2 ohm at $25^{o}C$, pH in between 6 and 7) was employed for all studies.

S2 - NMR parameters

All measures were operated with a Bruker UltraShield 400 spectrometer (Magnet System 400 MHz, 54 mm UltraShield Long Hold Time) at room temperature. A water pre-saturation method adjusted to the intensity of water signal, considering 10% D_2O and 90% H_2O proportion was applied. Shimming of the samples were performed using automatic shim program installed in the ICON-NMR software (Version 5.0.5). After which a 90° width pulse was applied and followed by FID acquisition. Spectral width (SW) was 20.02 ppm large (8012 Hz), with 64 kpt for ^1H and 240 ppm large (24 038 Hz), with 64 kpt for ^{13}C.

- peak position determination

For 1H NMR of each compound, 1.5 µL (if liquid) or 1.5 mg (if solid) is introduced in 2 mL of milliQ water (except when containing acid functional groups, see below). The NMR tube is prepared right after by mixing:

-48 µL of D_2O (10% volume)

-20 µL of internal reference solution (4 mM DMSO or 20 mM DSS).

-412 µL of investigated solution

Routine ^1H NMR measurement is then performed with pre-saturation method, d1 = 2 s and 32 scans.

For ^1H NMR chemical shifts, data have been recorded with DMSO as a reference, which position was set to 2.71 ppm. For some of them, signal record was repeated with 3-

(Trimethylsilyl)propane-1-sulfonate sodium salt (DSS) set as 0.00 ppm, giving consistent position ± 0.01 ppm.
For ^{13}C NMR chemical shifts, 40 µL (if liquid) or 40 mg (if solid) is introduced in 2 mL of milliQ water (except when containing acid functional groups, see below). The NMR tube is prepared right after by mixing:
-48 µL of D_2O (10% volume)
-40 µL of DMSO as internal reference.
-392 µL of investigated solution
After that, normal ^{13}C NMR measurement were performed with d1 = 2 s and 64 scans. Data have been recorded with DMSO as a reference, which position was set to 39.39 ppm. Data from the literature have been obtained either with TMS reference positioned at 0.00 ppm or methanol reference set at 49.50 ppm. When chemical shift values are reproduced from the ascribed references, precision of the values can vary from the above mentioned ± 0.01 ppm.

IMPORTANT: In the specific case of compounds containing acidic functional groups, the fully protonated form is recorded in 0.2 M HCl solution while the fully deprotonated is recorded in 0.1 M basic phosphate buffer (pH 12) with the exception of glycerate calcium that was dissolved in 0.1M KOH due to the precipitation of calcium phosphate. All other signal acquisitions have been made in milli-Q so that pH ranges between 6 to 7. For the chemical shift values taken from the literature, pH values are often varied from our experimental conditions but the values have been taken in the range predominant of chemical species of interest. Exact pH values can be found in the corresponding references.

In some particular cases in table 1, we report two $J_{C\text{-H}}$ values as they appear in ^1H NMR spectra.

- Quantification measurement (except formaldehyde)

NMR tubes are prepared by introducing:
-48 µL of D_2O (10% volume),
-40 µL of 4 mM internal reference solution (DMSO),
-392 µL of investigated solution.
Routine ^1H NMR measurement is then performed with pre-saturation method, d1 = 25 s and 128 scans.

Case of formaldehyde quantification

In this specific case, a slightly modified procedure was used. First, a solution of known concentration of HCHO is prepared (from 37% in water solution stabilized with 10-15% MeOH) and rigorously mixed with a fresh 1 M sodium bisulfite solution (50:50, v/v). Then the tube was prepared by introducing:
-48 µL of D_2O (10% volume),

-20 µL of 4 mM internal reference solution. Dimethylsulfone ($DMSO_2$) was selected since DMSO reacts with $NaHSO_3$ (see below).
-412 µL of prepared mixture solution.
Routine ^1H NMR measurement was then performed using pre-saturation method, d1 = 25 s and 16 scans. At lower concentration (50 µM HCHO case) more scans (128) and 40 µL of 20 mM $DMSO_2$ were instead used (Fig S2).
Because bisulfite is also known to react with carbon dioxide,[1] solution after electrolysis should be first bubbled with an inert gas such as Argon after electrolysis and fresh bisulfite should be used for each measurement since it is not stable for a long time.
1 M $NaHSO_3$ solution was used so that its pH predominates over the pH of the analyzed solution, as long as the latter is buffered to 0.1 M or below. In case of higher buffer concentration, a pH check is necessary before performing NMR measurement since the adduct formation is complete only when pH is in the range of predominance of HSO_3^- anion ($3.5 < pH < 5.5$). Then its value should be adjusted if necessary. Note also that in the specific case of a $NaHCO_3$ solution brought to basic pH, if too basic, carbonate can react with hydroxymethane sulfonate (adduct A, see main text), according to the following reaction.[2]

$$HOCH_2\text{-}SO_2Na + Na_2CO_3 \rightarrow CH_2O + Na_2SO_3 + NaHCO_3$$

S3 – Product concentration quantification

On NMR spectrum, phase is corrected so that baseline lies flat around both internal standard and peak of interest. A straight baseline is then applied so that integration is nil at both extremities of the integral.
Concentration in the tube is then calculated from classical equation:

$$C_{product\ of\ interest,\ tube} = C_{internal\ standard,\ tube} \frac{\frac{I_{product\ of\ interest}}{H_{product\ of\ interest}}}{\frac{I_{internal\ standard}}{H_{internal\ standard}}}$$

C: concentration
I: Intensity of the peak
H: Protons per molecule attributed to the peak
From concentration in the tube, concentration in the electrolyte is obtain through simple cross-multiplication and then multiply by the volume of electrolyte to get the total production of the compound.

S4 - DMSO and $DMSO_2$ stability in presence of bisulfite

Both DMSO and $DMSO_2$ have been introduced in an NMR tube in presence of 0.05 M $NaHSO_3$ and methanol as internal standard since this alcohol is known to be stable in presence of bisulfite.[1] In these conditions, DMSO peak is modified after 24h (Fig. S1 a and b) while another peak has appeared at around 2.09 ppm. When same experiment is performed with $DMSO_2$, the peak intensity is highly steady even after 48h (Fig. S1 c and d).

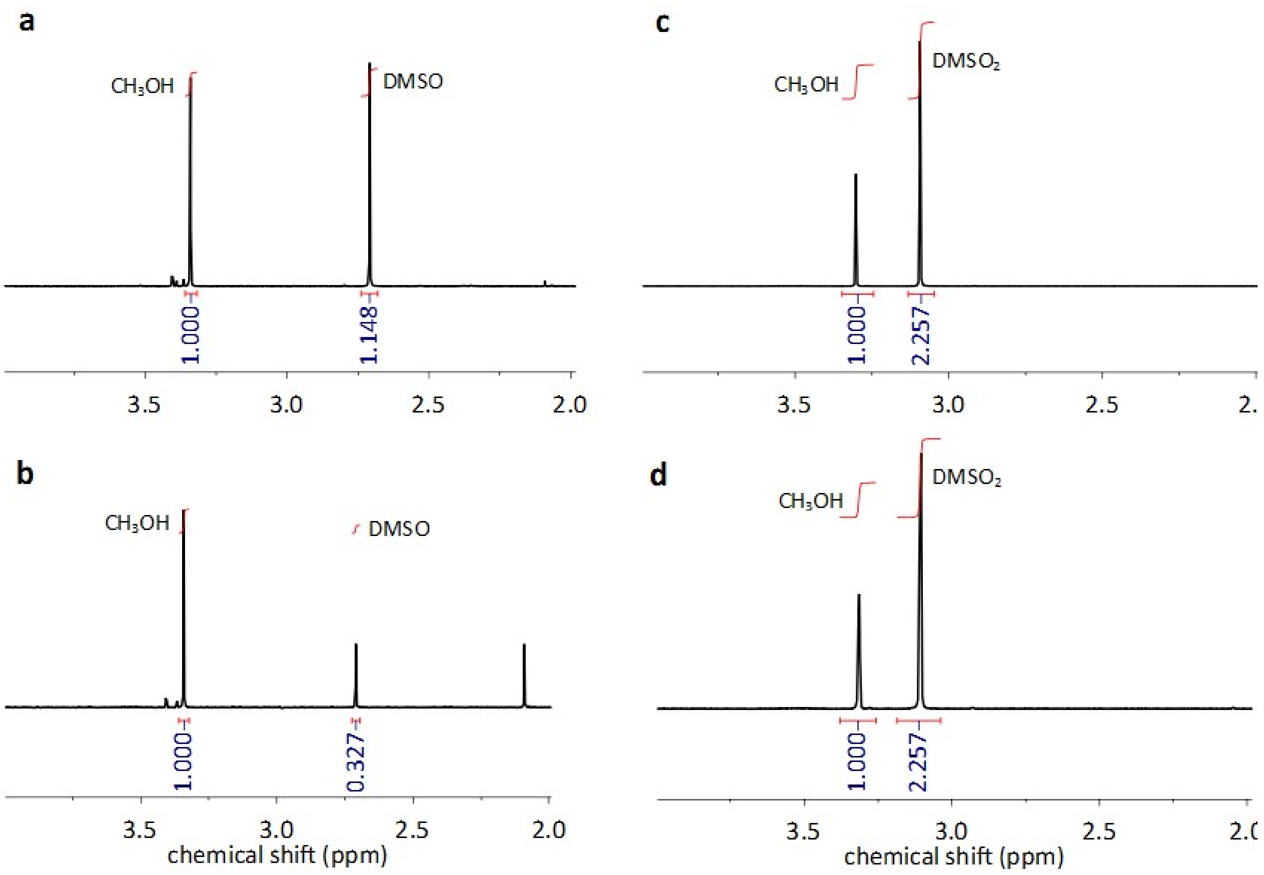


Fig. S1 Peak intensity of DMSO vs. CH_3OH reference (a and b) in presence of 0.05 M $NaHSO_3$ right after filling the tube (a) and after 24h (b). Same experiment with $DMSO_2$ (c and d) versus CH_3OH reference in presence of 0.05 M $NaHSO_3$, right after filling the tube (c) and after 48h (d).

S5 - HCHO quantification spectra using $DMSO_2$ as internal standard

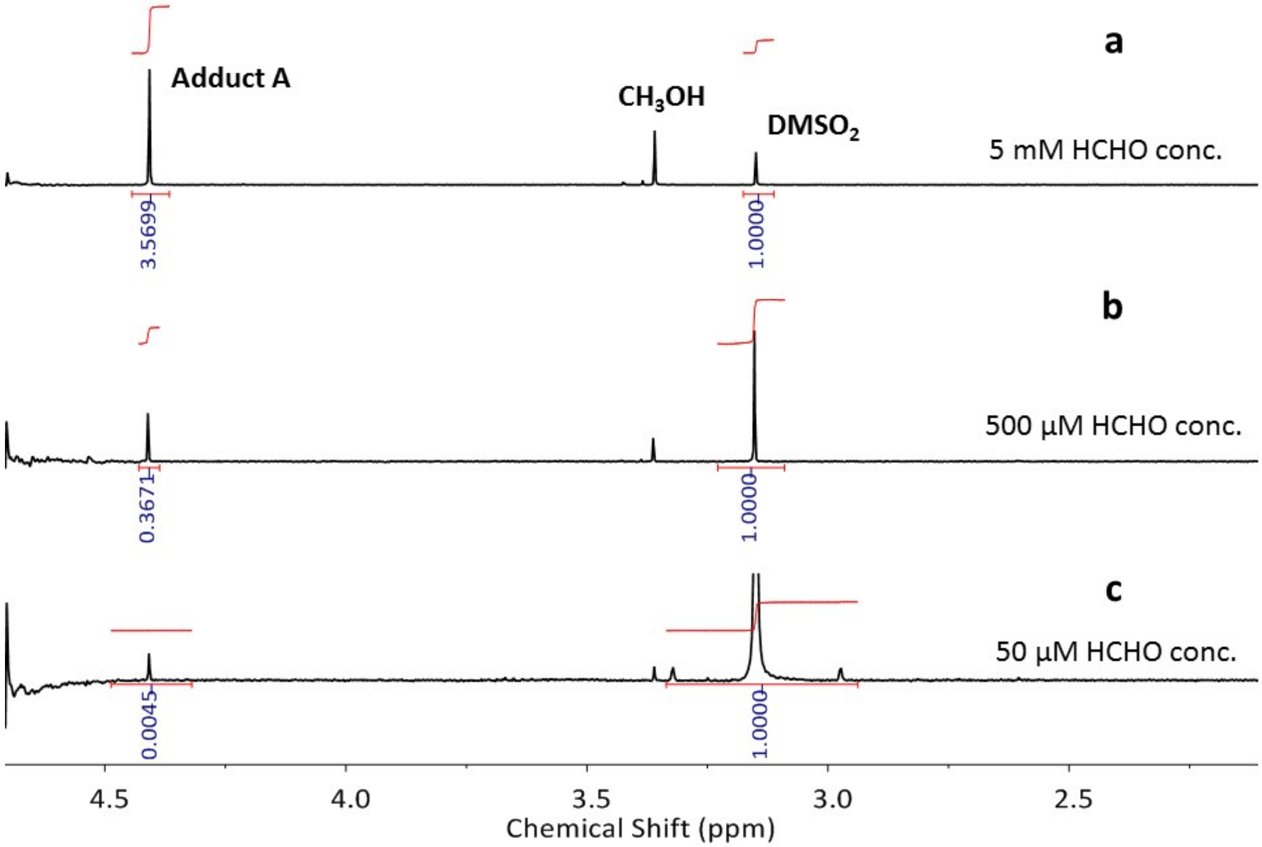
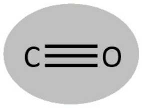


Fig. S2 Peak intensity of Adduct A vs. $DMSO_2$ reference after addition step, for three starting concentrations of HCHO. (a) 5 mM, (b) 500 µM and (c) 50 µM.

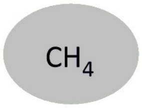
S6 - List of possible CO_2RR products

The following compounds are representing possible products of the type $C_xO_yH_z$, with x being 1, 2 or 3. Depending on the possibility or not to record ^1H NMR of these products, different colors are assigned. Recorded (green), not recorded but reported from bibliography (blue), no proton recorder due to absence of visible proton in water but ^{13}C NMR value reported (red), not recorded because gaseous (gray), not recorded because unstable or not available commercially (orange). For acids compounds we also recoded NMR spectra for the corresponding conjugate base. In most cases the 1H NMR data has been recorder while ^{13}C value has been taken from literature. In such case, the reference is only given in the ^{13}C column. When data for both ^1H NMR and ^{13}C NMR has been taken from literature, reference is given for the full line, next the molecule name.

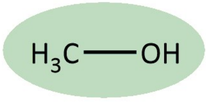
Possible C_1 products



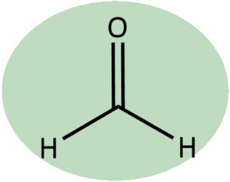
carbon monoxide



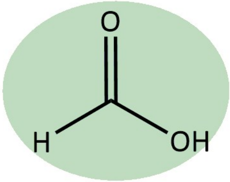
methane



methanol

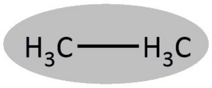


formaldehyde

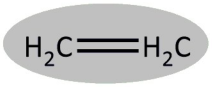


formic acid

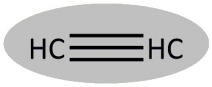
Possible C_2 products



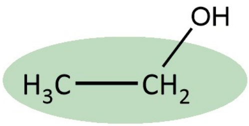
ethane



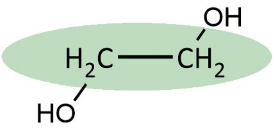
ethene



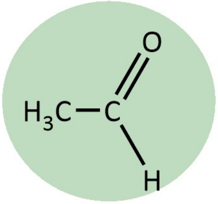
ethyne



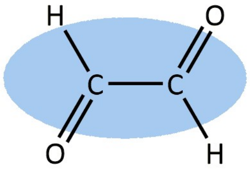
ethanol



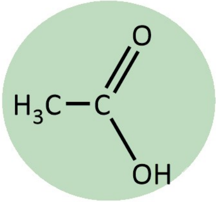
ethane-1,2-diol
or
ethylene glycol



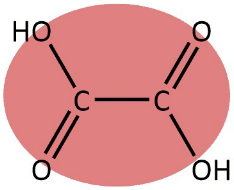
acetaldehyde



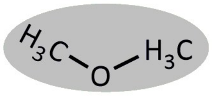
oxalaldehyde
or
glyoxal



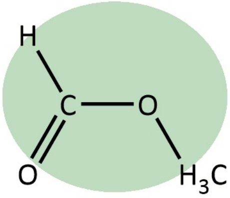
acetic acid



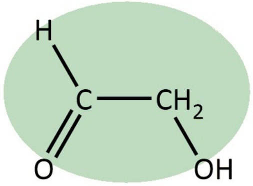
oxalic acid



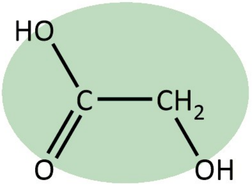
dimethyl ether



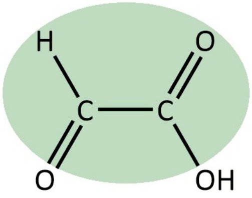
methyl formate



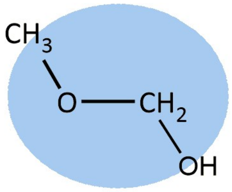
2-hydroxyacetaldehyde
or
glycolaldehyde



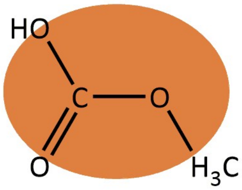
2-hydroxyacetic acid
or
glycolic acid



2-oxoacetic acid
or glyoxylic acid



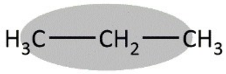
methoxymethanol



methyl hydrogen
carbonate

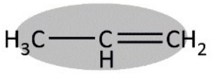
Possible C_3 products

Alkane

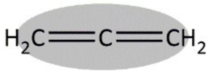


propane

Alkene

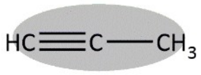


prop-1-ene



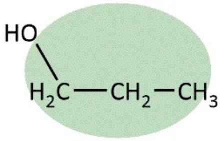
propa-1,2-diene

Alkyne

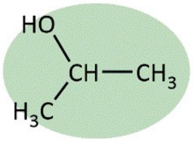


prop-1-yne

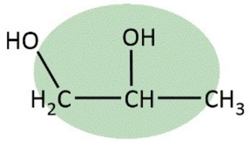
Alcohol



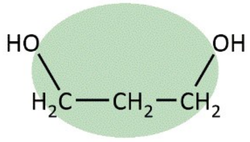
propan-1-ol



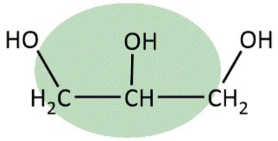
propan-2-ol
or
isopropanol



propane-1,2-diol
or
propylene glycol

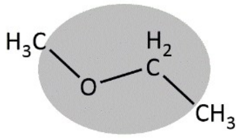


propane-1,3-diol

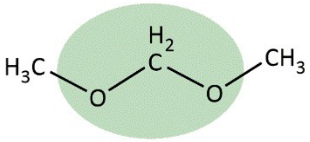


propane-1,2,3-triol
or glycerol

Ether

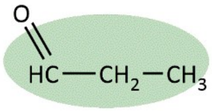


methoxyethane

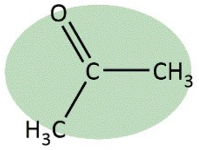


dimethoxymethane

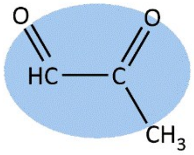
Carbonyl



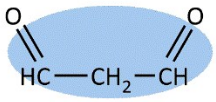
propionaldehyde



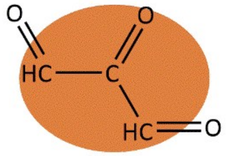
propan-2-one
or
acetone



2-oxopropanal
or methylglyoxal

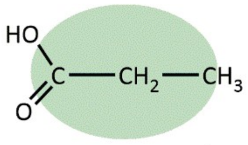


malonaldehyde

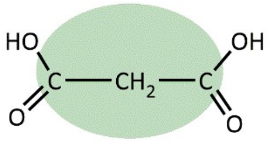


2-oxomalonaldehyde

Acid

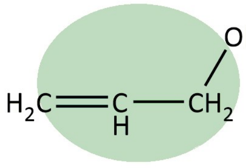


propionic acid

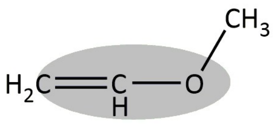


malonic acid

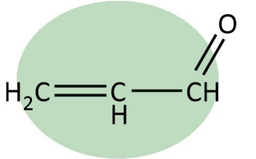
Combinations



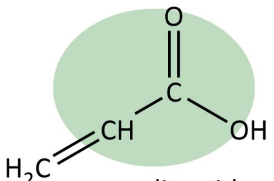
prop-2-en-1-ol
or
Allyl alcohol



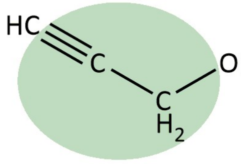
methoxyethene



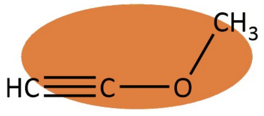
acrylaldehyde
or
Acrolein



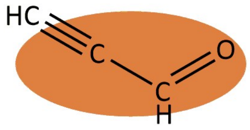
acrylic acid



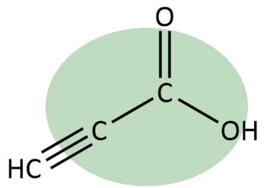
prop-2-yn-1-ol
or
Propargyl alcohol



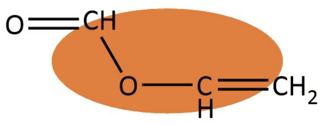
methoxyethyne



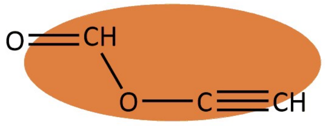
propiolaldehyde



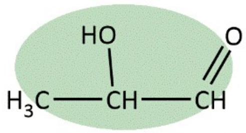
propiolic acid



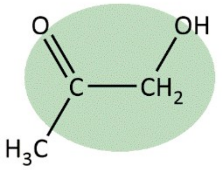
vinyl formate



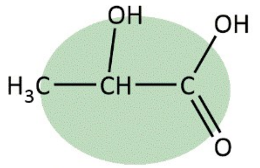
ethynyl formate



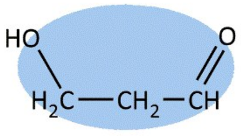
2-hydroxypropanal
or
Lactaldehyde



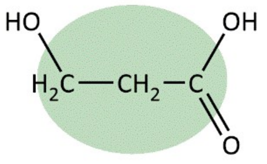
1-hydroxypropan-2-one
or
Hydroxyacetone



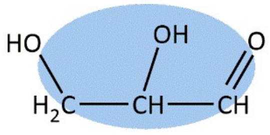
2-hydroxypropanoic acid
or Lactic acid



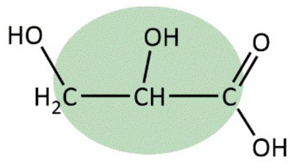
3-hydroxypropanal
or Reuterin



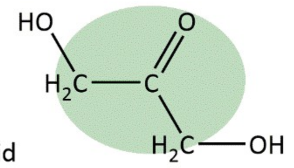
3-hydroxypropanoic acid



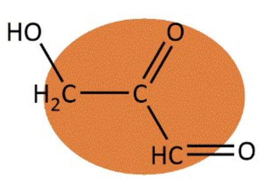
2,3-dihydroxypropanal
or Glyceraldehyde



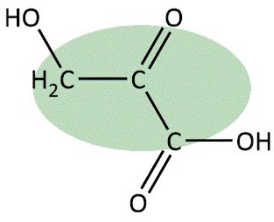
2,3-dihydroxypropanoic acid
or Glyceric acid



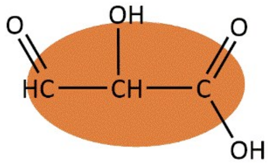
1,3-dihydroxypropan-2-one
Or dihydroxyacetone



3-hydroxy-2-oxopropanal

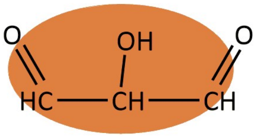


3-hydroxy-2-oxopropanoic acid
Or Beta-hydroxypyruvic acid

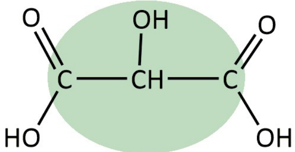


2-hydroxy-3-oxopropanoic acid
Or tartronate semialdehyde

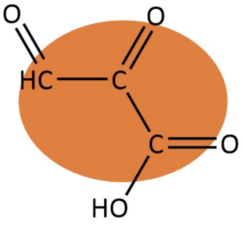
Combination (continued)



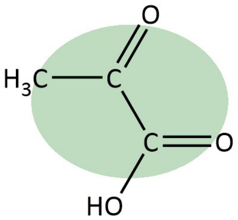
2-hydroxymalonaldehyde
Or glucic acid



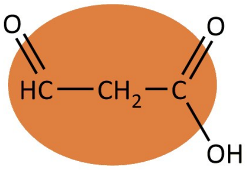
2-hydroxymalonic acid
Or tartronic acid



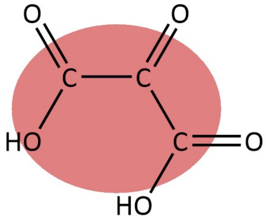
2,3-dioxopropanoic acid



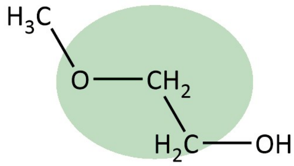
2-oxopropanoic acid
or
pyruvic acid



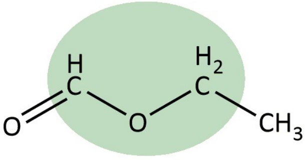
3-oxopropanoic acid



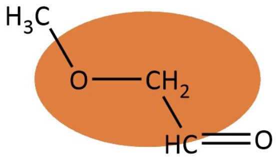
2-oxomalonic acid
or mesoxalic acid



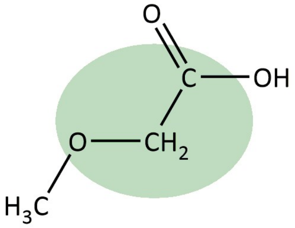
2-methoxyethanol



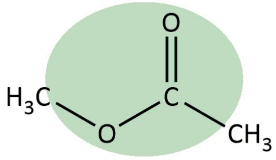
ethyl formate



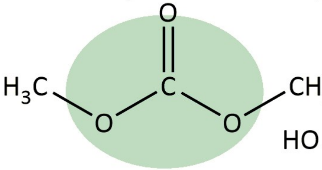
2-methoxyacetaldehyde



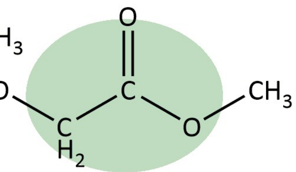
2-methoxyacetic acid



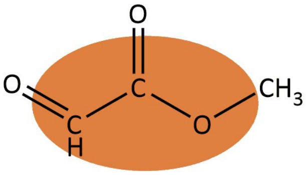
methyl acetate



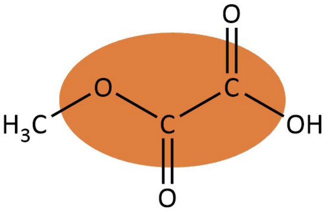
dimethyl carbonate



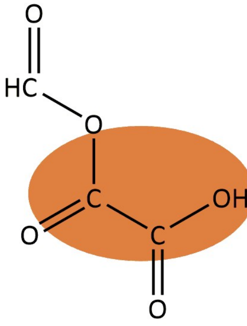
methyl 2-hydroxyacetate
or
Methyl glycolate



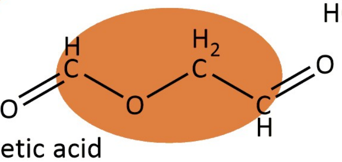
methyl 2-oxoacetate



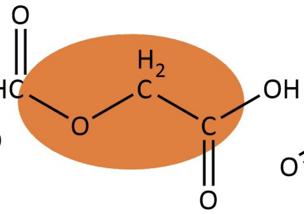
2-methoxy-2-oxoacetic acid



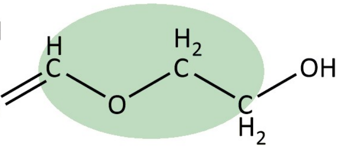
2-(formyloxy)-2-oxoacetic acid



2-oxoethyl formate

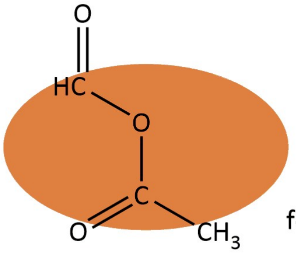


2-(formyloxy)acetic acid

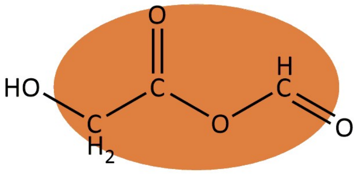


2-hydroxyethyl formate

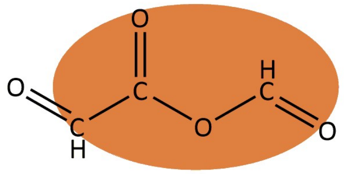
Combination (continued)



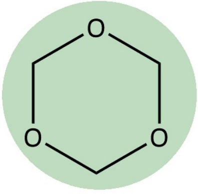
acetic formic anhydride



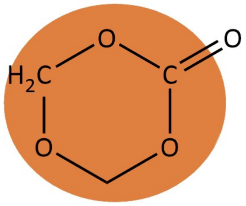
formic 2-hydroxyacetic anhydride



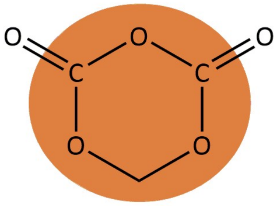
formic 2-oxoacetic anhydride



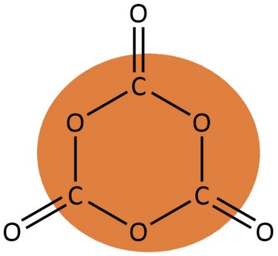
1,3,5-trioxane



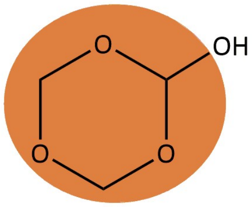
1,3,5-trioxan-2-one



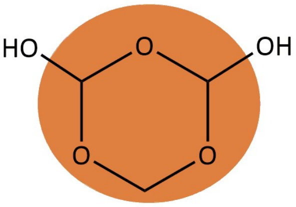
1,3,5-trioxane-2,4-dione



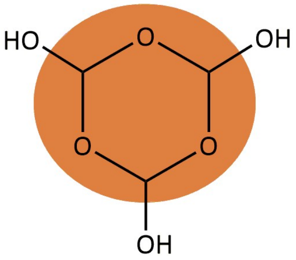
1,3,5-trioxane-2,4,6-trione



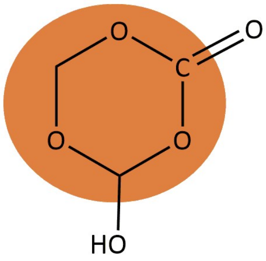
1,3,5-trioxan-2-ol



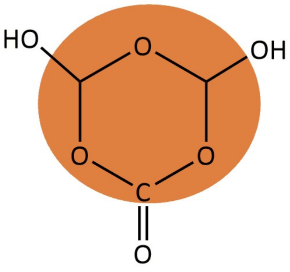
1,3,5-trioxane-2,4-diol



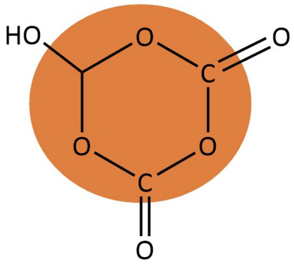
1,3,5-trioxane-2,4,6-triol



4-hydroxy-1,3,5-trioxan-2-one



4,6-dihydroxy-1,3,5-trioxan-2-one



6-hydroxy-1,3,5-trioxane-2,4-dione

SI References

1. J. F. Walker, in *Formaldehyde - Monograph series no. 159*, 1964, pp. 483-510.
2. A. Gardziella, L. A. Pilato and A. Knop, 2000, p. 502.