K^+ selectivity modulation in non-aqueous CO_2 electroreduction on lead catalyst: from oxalic to tartaric acid production

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Table S1: Inductively coupled plasma-optical emission spectroscopy (ICP-OES) results for the non-aqueous catholyte after 30 min of electrolysis using different anolytes.

Anolyte	**Element concentration (ppm)**	
	Pb	**K**
H_2SO_4	0.315	0.016
$KHCO_3$	0.350	247.297
KOH	0.989	566.325

Table S2: Simulated value for impedance and resistance before and after cyclic voltammetry cleaning process for each anolyte.

Anolyte	R1 (Ω cm^2)	R2 (Ω cm^2)	R3 (Ω cm^2)	CPE1		CPE2	
				CPE (T)	CPE (P)	CPE (T)	CPE (P)
Before Cyclic Voltammetry Cleaning Activation							
H_2SO_4	5.42	208	-	$7.38x10^{-5}$	0.90	-	-
$KHCO_3$	3.59	7.88	182.2	0.02	0.37	$1.37\ x10^{-6}$	0.878
KOH	5.04	87.43	-	$1.14\ x10^{-4}$	0.86	-	-
After Cyclic Voltammetry Cleaning Activation							
H_2SO_4	4.15	78.70	245.60	$3.7x10^{-4}$	0.76	$7.48x10^{-5}$	0.97
$KHCO_3$	3.99	14.77	221.3	0.003	0.55	$7.38x10^{-5}$	0.92
KOH	5.75	58.66	-	$1.08\ x10^{-4}$	0.86	-	-

Figure S1: a) Equivalent electrical circuit used for modelling the Pb plate electrode in CO_2-saturated acetonitrile (0.1 M $TBAPF_6$) with $KHCO_3$ anolyte before and after the cyclic cleaning process and H_2SO_4 after cleaning process. **b)** The equivalent electrical circuit for the Pb plate with H_2SO_4 before the cyclic voltammetry cleaning process and KOH before and after cyclic cleaning.

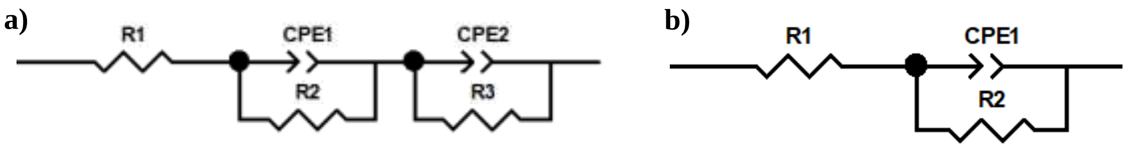

Figure S2: Cyclic voltammogram for Pb plate electrode at dried acetonitrile 0.1 M $TBAPF_6$ saturated with CO_2 using H_2SO_4, $KHCO_3$, and KOH as analyte and a scan rate of 20 mV/sec.

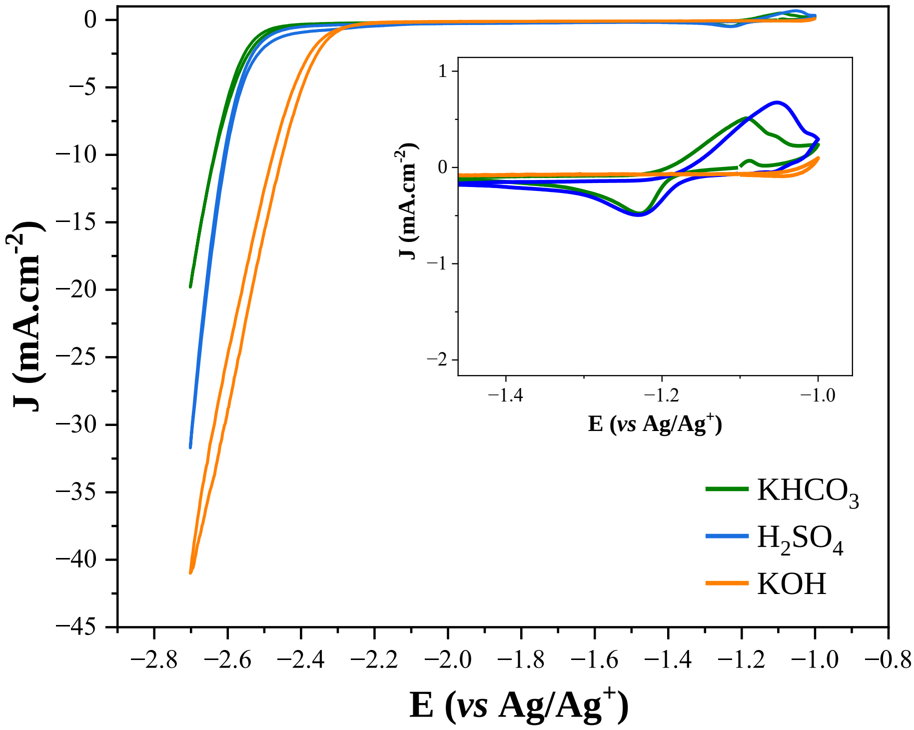

Figure S3: a) HPLC-UV calibration curve for the determination of formic acid (0.1–25 mol mL^{-1}) water pH 3 (H_2SO_4) as mobile phase with flow rate of 0.6 mL/min and sample injection volume of 20 µL and **b)** HPLC chromatogram for each concentration.

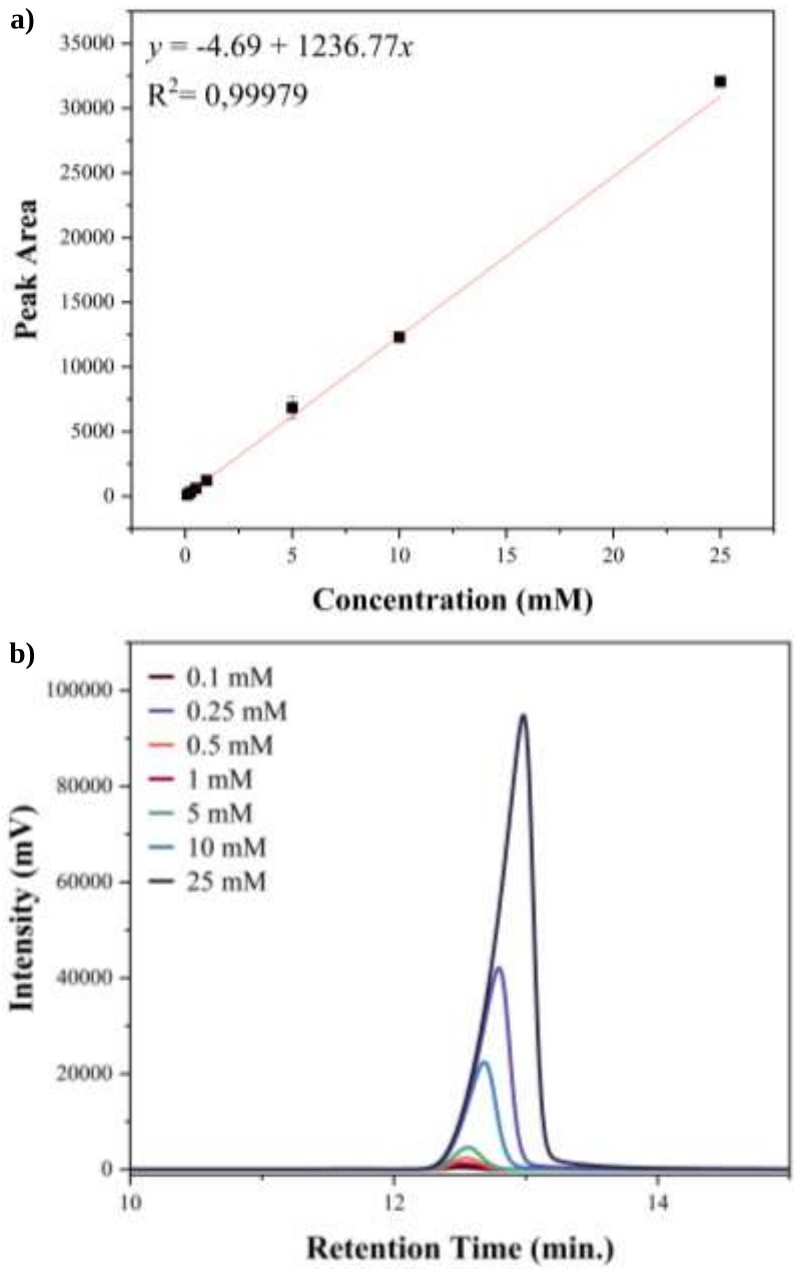

Figure S4: a) HPLC-UV calibration curve for the determination of oxalic acid (0.1–5 mol mL^{-1}) water pH 3 (H_2SO_4) as mobile phase with flow rate of 0.6 mL/min and sample injection volume of 20 µL and **b)** HPLC chromatogram for each concentration.

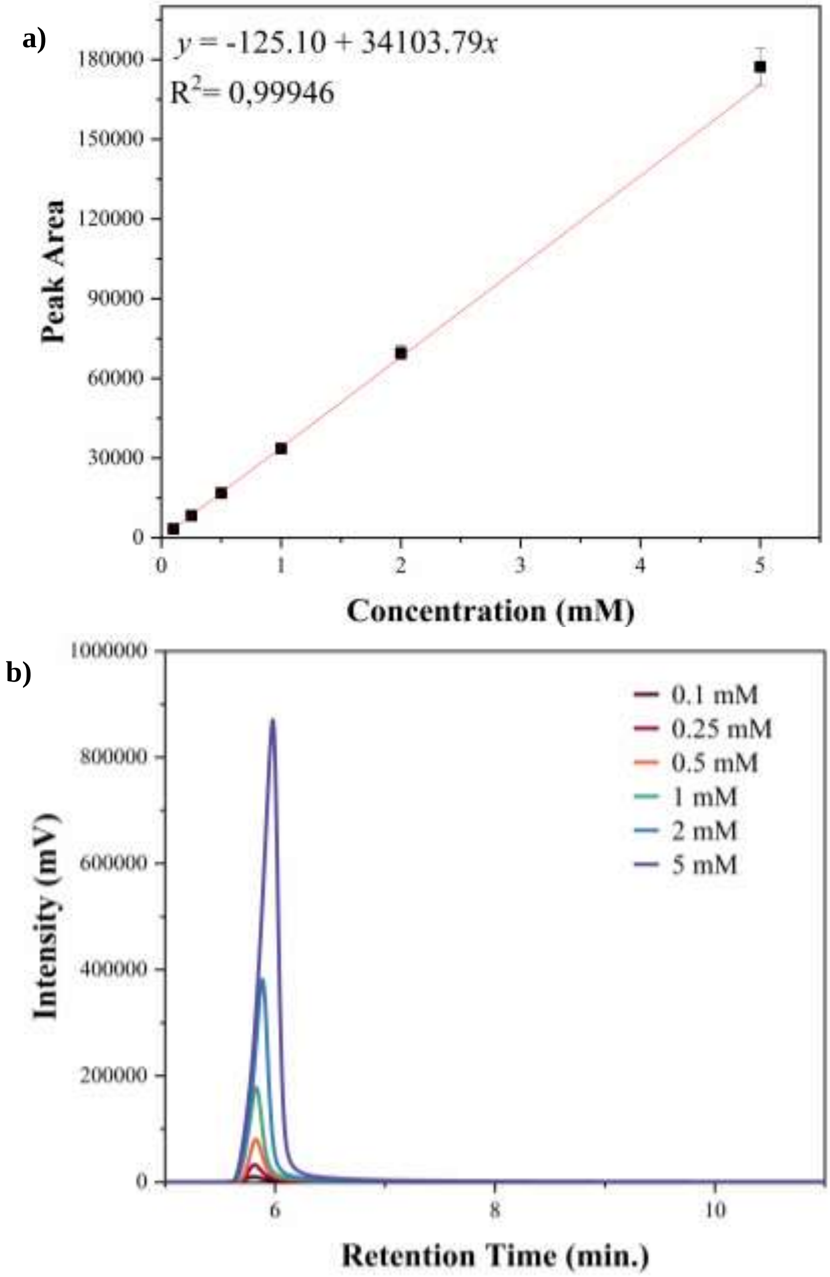

Figure S5: a) HPLC-UV calibration curve for the determination of oxalic acid (0.1–0.5 mol mL^{-1}) water pH 3 (H_2SO_4) as mobile phase with flow rate of 0.6 mL/min and sample injection volume of 20 µL and **b)** HPLC chromatogram for each concentration.

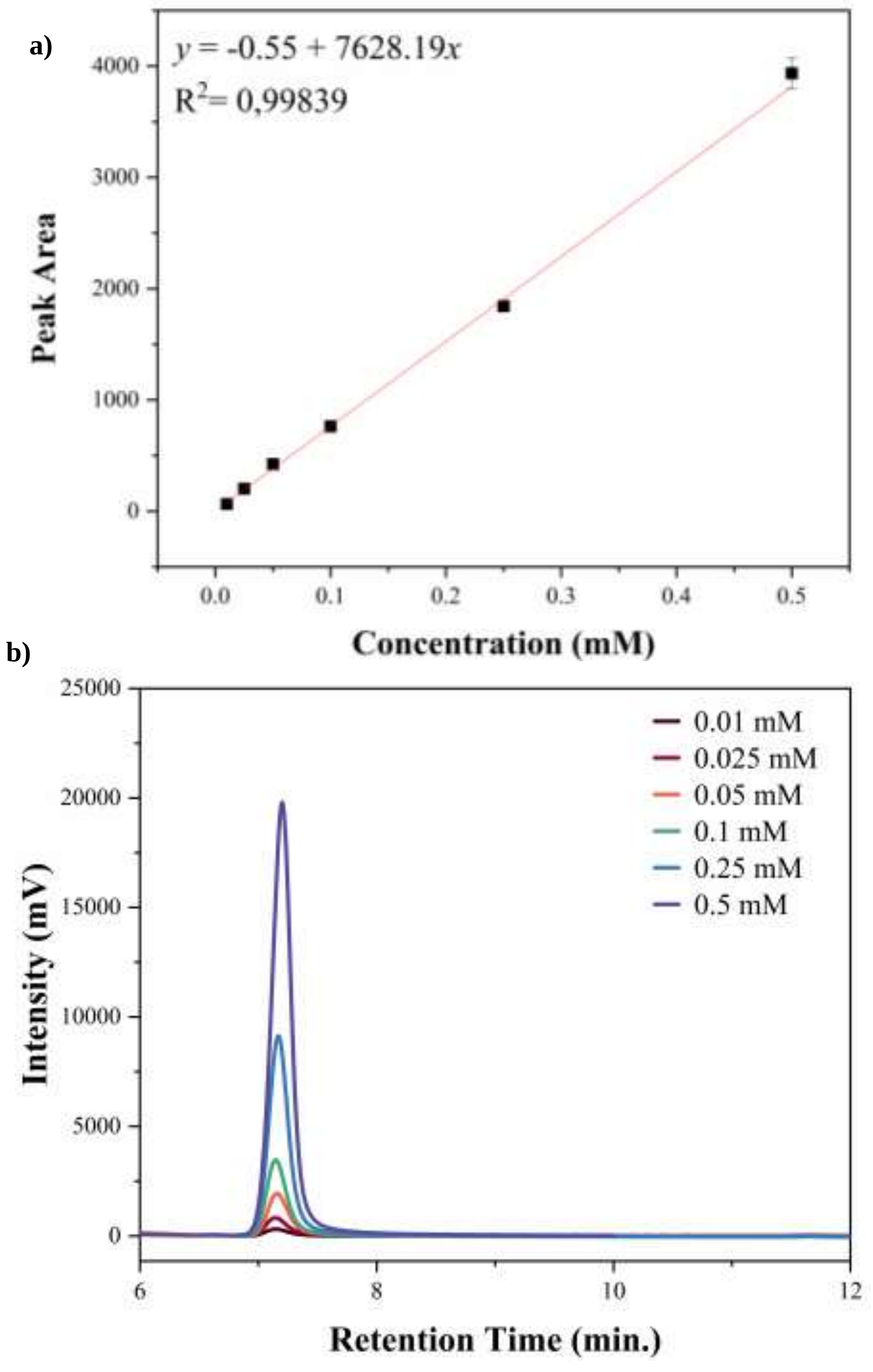

Figure S6: HPLC chromatogram of the electrolysis sample using each anolyte (H_2SO_4, $KHCO_3$ and KOH). A: Oxalic acid; B: Tartaric acid; C: Formic acid.

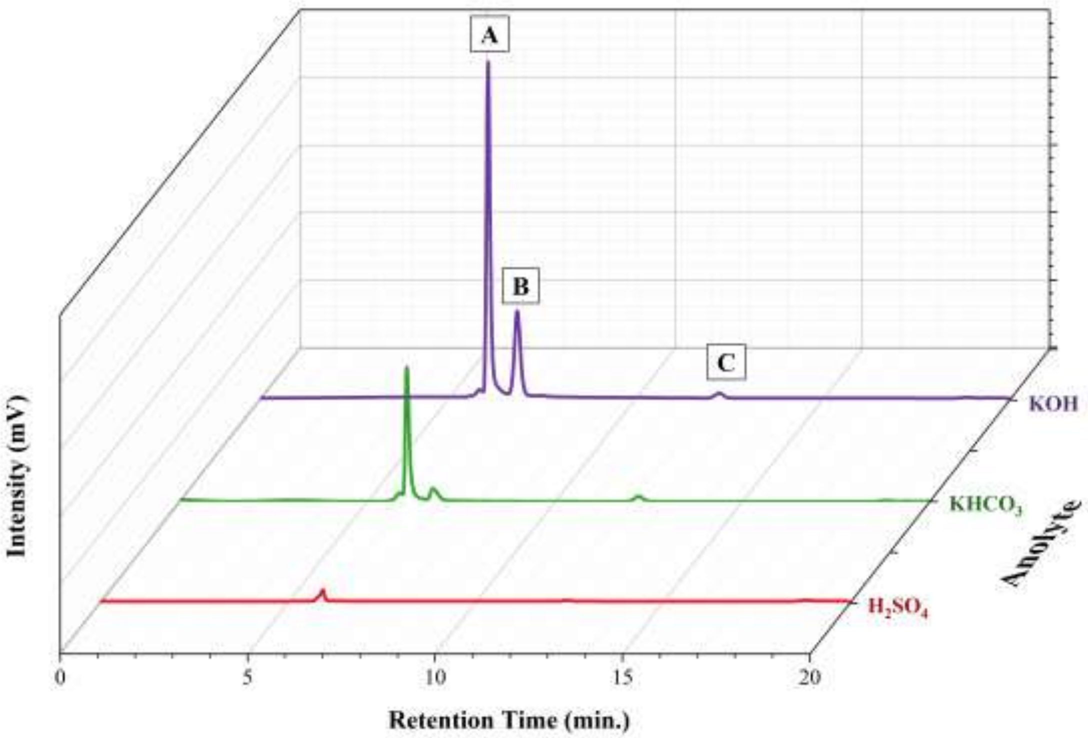

Table S3: Comparison of previous literature studies of Pb and Pb-based electrocatalysts for CO_2RR in organic media with the products and the faradaic efficiency.

Electrode	Catholyte	Anolyte	Major products	Cathode Potential or j applied	FE (%)	Ref.
Pb Plate	0.1 M Bu_4NPF_6/AN	1.0 M KOH	$C_4H_4O_6^{2-}$ and $C_2O_4^{2-}$	-2.3 V vs Ag/Ag	60 ($C_4H_4O_6^{2-}$) 30 ($C_2O_4^{2-}$)	This Work
Pb	0.3 M Et_4NClO_4/PC	0.1 M H_2SO_4/H_2O	$H_2C_2O_4$	2.7 V *vs.* Ag/Ag$^+$	10 ($H_2C_2O_4$)	1
Pb	0.1 M Bu_4NClO_4/PC	See catholyte	$H_2C_2O_4$	2.8 V *vs.* Ag/AgCl	76 ($H_2C_2O_4$)	2
Pb sheet	0.1 M Bu_4NClO_4/AN	See catholyte	$C_2O_4^{2-}$	2.4 V *vs.* Ag/Ag$^+$	73 ($C_2O_4^{2-}$)	3
	0.1 M [emim][Tf_2N] /AN	See catholyte	CO	2.25 V *vs.* Ag/Ag$^+$	45 (CO)	
Pb sheet	0.9 M [TEA][4-MF-PhO]/AN	0.1 M H_2SO_4	$H_2C_2O_4$	2.6 V *vs.* Ag/Ag$^+$	86 ($H_2C_2O_4$)	4
	0.1 M Bu_4NBF_4/AN	0.1 M H_2SO_4	HCOOH and $H_2C_2O_4$	2.6 V *vs.* Ag/Ag$^+$	67 (HCOOH) 20 ($H_2C_2O_4$)	
Pb sheet	0.1 M Bu_4NPF_6/AN	0.1 M H_2SO_4	CO, HCOOH, and $H_2C_2O_4$	2.6 V *vs.* Ag/Ag$^+$	21 (CO) 66 (HCOOH) 11 ($H_2C_2O_4$)	
	0.1 M [BMIM][BF4]/ AN	0.1 M H_2SO_4	CO and HCOOH	2.6 V *vs.* Ag/Ag$^+$	17 (CO) 80 (HCOOH)	
Pb powder	0.25 M Bu_4NBF_4/AN (CO_2 supplied at the back of the GDE)	See catholyte	$C_2O_4^-$ and CO	20-80 mA.cm^2	At –80 mA.cm^2: 53 ($C_2O_4^-$)	5
Pb wire	0.7 M Et_4NCl/PC	0.5 M H_2SO_4	$H_2C_2O_4$, $C_2H_4O_3$, and HCOOH	2.5 V *vs.* Ag/AgCl	71 ($H_2C_2O_4$) 3 ($C_2H_4O_3$) 7 (HCOOH)	6
	0.1 M Et_4NCl/AN	0.5 M H_2SO_4	$H_2C_2O_4$ and HCOOH	2.5 V *vs.* Ag/AgCl	6 ($H_2C_2O_4$) 82 (HCOOH)	

	0.1 M Bu_4NClO_4/PC	0.5 M H_2SO_4	$H_2C_2O_4$ and HCOOH	2.6 V *vs.* Ag/AgCl	39 ($H_2C_2O_4$) 38 (HCOOH)	
Pb plate	0.7 M Et_4NCl/PC	0.5 M H_2SO_4	$H_2C_2O_4$, $C_2H_2O_3$, $C_2H_4O_3$ and HCOOH	2.3, 2.4 and 2.7 V *vs.* Ag/AgCl	At –2.3 V: 75 ($H_2C_2O_4$) 20 (HCOOH)	
MoO_2/Pb	0.1 M Bu_4NPF_6/AN	See catholyte	$H_2C_2O_4$ and HCOOH	2.3 - 2.6 V *vs.* Ag/Ag^+	At –2.6 V: 44 ($H_2C_2O_4$) 5.4 (HCOOH)	7
PbO/C	0.1 M Bu_4NClO_4/AN	See catholyte	$C_2O_4^{2-}$ and CO	1.7 - 2.5 V *vs.* Ag/Ag^+	At –2.2 V: 50 ($C_2O_4^{2-}$) 45 (CO)	
$PbSnO_3$/C	0.1 M Bu_4NClO_4/AN	See catholyte	$C_2O_4^{2-}$	1.7 - 2.5 V *vs.* Ag/Ag^+	At –1.9 V: 85 ($C_2O_4^{2-}$)	8
$Pb_3Sn_1O_x$/C	0.1 M Bu_4NClO_4/AN	See catholyte	$C_2O_4^{2-}$	1.8 – 2.4 V *vs.* Ag/Ag^+	At –2.3 V 73($C_2O_4^{2-}$)	
$Pb_1Sn_3O_x$/C	0.1 M Bu_4NClO_4/AN	See catholyte	$C_2O_4^{2-}$	1.8 – 2.4 V *vs.* Ag/Ag^+	At –2.2 V: 61 ($C_2O_4^{2-}$)	
Pb wire	0.56 M KCl/MeOH	0.56 M H_2O	$C_2H_4O_2$ and HCOOH	2.0 V vs. Ag/AgCl	75 ($C_2H_4O_2$) 15 (HCOOH)	9
Pb	Sat. KCl + 0.03 M HCl/MeOH	0.05 M H_2SO_4	$C_2H_4O_2$	20 $mA.cm^{-2}$	97 ($C_2H_4O_2$)	10

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