Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Direct, *in situ* Determination of pH and Solute Concentrations in Formic Acid Dehydrogenation and CO_2 Hydrogenation in Pressurised Aqueous Solutions Using ^{1}H and ^{13}C NMR Spectroscopy

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Experimental Part

0.100 M solutions of carbonate/bicarbonate and formate/formic acid were prepared by dissolving Na_2CO_3, $NaHCO_3$ or HCOONa, or by diluting HCOOH, depending on the desired pH of the sample. The pH values of the NMR samples were determined directly in the NMR tube using a pH meter with calibrated glass electrode, by pH calculation, by the NMR method developed. The pH of the solution was adjusted by dissolving CO_2 gas in the solution or by adding HCl and NaOH.

Measurements of the chemical shifts and spin-lattice T_1 relaxation time of CO_3^{2-} and $HCOO^-$ were performed on a Bruker DRX 400 NMR spectrometer. 99% enriched ^{13}C Na_2CO_3, $NaHCO_3$, HCOONa and HCOOH were used for the ^{13}C NMR spectroscopic studies.

^{13}C and ^{1}H relaxation time

The spin-lattice relaxation time (T_1) of formic acid, formate, carbonate, bicarbonate and carbon dioxide were determined using the standard 180° - vd (variation delay) – 90° inversion recovery pulse sequence[1]. A 90° pulse length of 13.5 μs with 18 experiments of 4 scans was used for ^{13}C NMR spectra. The ^{1}H NMR studies were carried out using 90° pulse lengths of 15 μs with 16 experiments of 4 scans. Studies of the pH dependence on the relaxation time were performed at temperatures between 23 °C and 70 °C for ^{13}C NMR spectra, and between 23 °C and 50 °C for ^{1}H NMR spectra. Determination of the relaxation rate was verified by fitting the corresponding peak intensity as a function of the recovery time using WIN-NMR[2].

[1] a)T. C. Farrar, B. Becker, *Pulse and Fourier Transform NMR*, New York, **1971**; b)R. R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford, **1987**.

[2] Program library, developed at ISIC, EPFL.

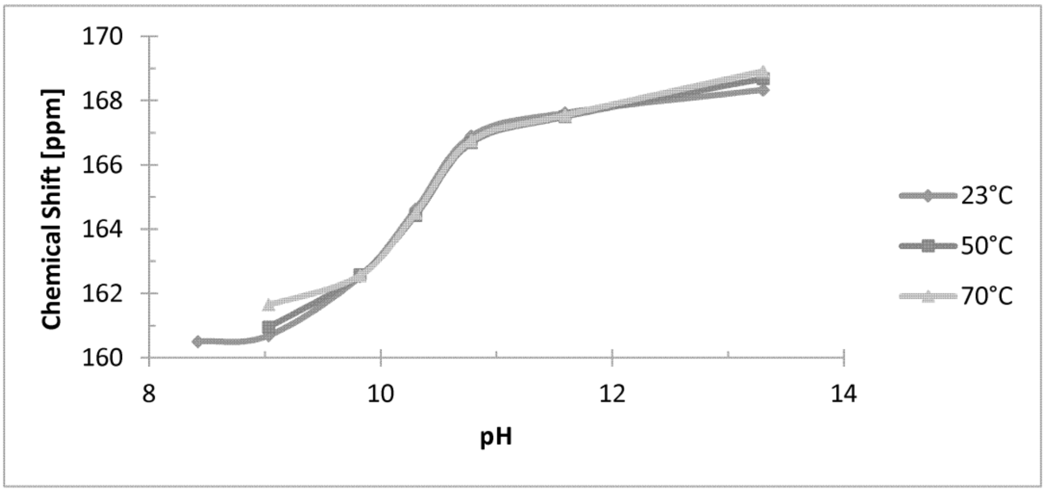

Fig.S1 Calibration curve of the ^{13}C NMR chemical shift of HCO_3^-/CO_3^{2-} as function of pH and temperature (c_{total} = 0.10 M). Average values of several (2-4) measurements, reproducibility is ± 0.1 ppm

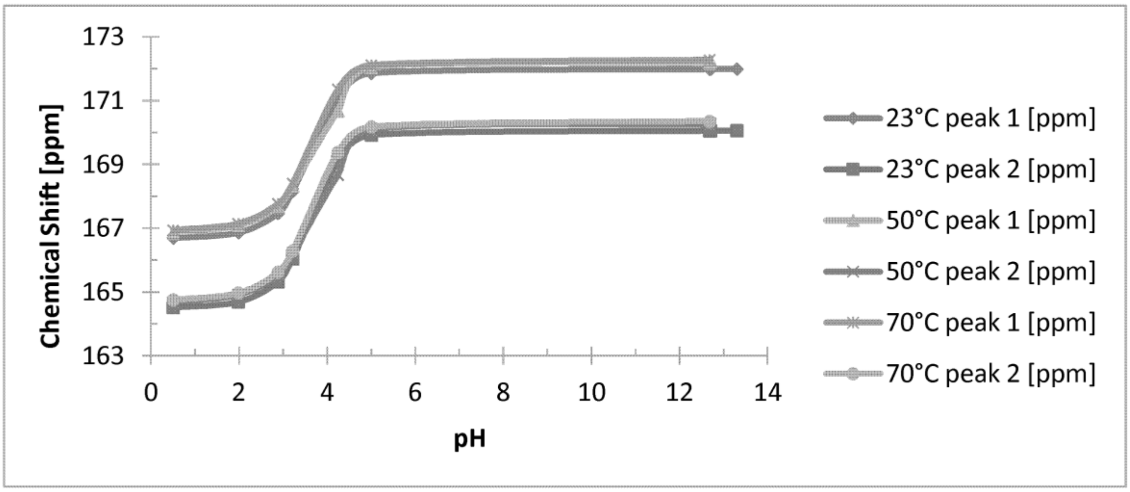

Fig.S2 Calibration curve of the ^{13}C NMR chemical shift of $HCOO^-/HCOOH$ $^-$ as function of pH and temperature (c_{total}= 0.10 M). Average values of several (2-4) measurements, reproducibility is ± 0.1 ppm

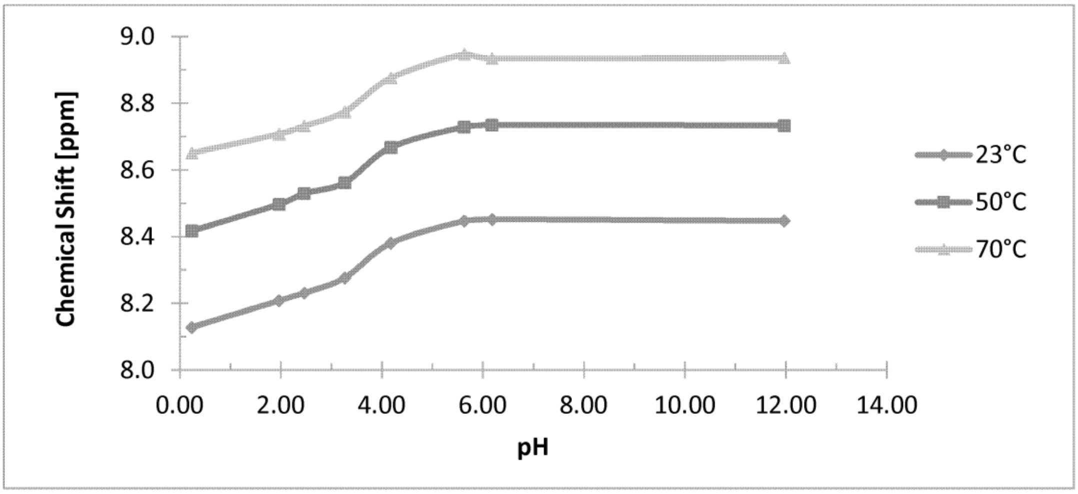

Fig.S3 Calibration curve of the ^{1}H NMR chemical shift of $HCOO^-/HCOOH$ $^-$ as function of pH and temperature (c_{total} = 0.10 M). Average values of several (2-4) measurements, reproducibility is ± 0.01

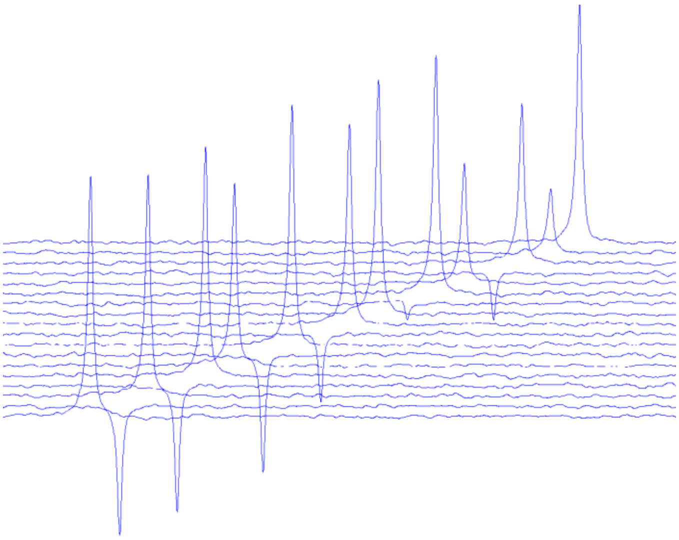

Fig.S4 ^{13}C NMR singlet (c_{total} = 0.1 M) chemical shift of $H^{*}CO_3^{-}/^{*}CO_3^{2-}$ in the fast exchange domain for a solution of pH 11. By the use of the inversion recovery experiment with a variation delay (vd) list of 600, 0.01, 80, 0.1, 100, 50, 1, 200, 5, 60, 125, 10, 150, 30, 7, 40, 20 and 300s.

A standard solution of 0.22 M ethanol was prepared by the addition of 0.40 mL ethanol in 36 mL water (concentration determined by the weight of water and ethanol). The 3 samples were prepared by the respective dilution of HCOONa and HCOOH addition in the aqueous ethanol solution (Table T1). The resulting samples were analysed by ^{1}H NMR spectrometry with a relaxation time of 100 s.

Table S1 Determination of the $HCOO^-$/HCOOH concentration by ^{1}H NMR spectroscopy.

Entry	HCOONa [g]	HCOOH [g]	Ethanol solution [g]	Ethanol [M]	HCOOH+$HCOO^-$ calculated [M]	HCOOH+$HCOO^-$ determined [M]
1	-	1.11	9.98	0.22	2.36	2.38
2	0.75	0.64	10.5	0.22	2.34	2.38
3	0.76	-	5.18	0.22	2.14	2.10

A standard solution of 0.31 M ethanol was prepared by the addition of 0.2 mL ethanol in 18 mL D_2O (concentration determined by the weight of D_2O and ethanol). The 3 samples were prepared by the respective dilution of $NaHCO_3$ and /Na_2CO_3 in the aqueous ethanol solution (Table T2). The resulting samples were analysed by ^{13}H NMR spectrometry with different delay time, depending of the pH of the solution. .

Table S2 Determination of the $NaHCO_3$/Na_2CO_3 concentration by ^{13}C NMR spectroscopy.

Entry	Delay time (D_1) [s]	Na_2CO_3 [g]	$NaHCO_3$ [g]	Ethanol solution [g]	CO_3^{2-} calculated [M]	CO_3^{2-} determined [M]
1	900	0.23	-	5.65	0.42	0.40
2	600	0.13	0.10	5.64	0.47	0.47
3	100	-	0.18	5.65	0.41	0.39