CO_2 Activation

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Selective Formic Acid Synthesis from Nanoscale Electrochemistry**

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Formic acid is a promising hydrogen storage material.[1] While efficient ways of releasing hydrogen from formic acid have been demonstrated, its energy-efficient and selective synthesis is still a challenge.[2] Although the electrochemical reduction of carbon dioxide to formic acid has been known since 1870,[3] current research is dedicated to optimizing the energy efficiency and selectivity of the reaction.[4–6] A major problem is poisoning of the electrodes with adsorbed CO.[5] Herein, we report a mechanistic study on the selective hydrogen-atom transfer (HAT) from methyl mercaptan to the aqueous $CO_2^{\bullet-}$ radical anion. HAT from thiol groups to $CO_2^{\bullet-}$ has been reported previously for β-mercaptoethanol, penicillamine, lipoamide, and 1,4-dimercaptobenzene in pulse radiolysis studies.[7] This reaction coupled to electrochemical activation of CO_2 in a tailor-made nanoscale environment may help to achieve the selective synthesis[6] of formic acid.

Carbon dioxide reacts with hydrated electrons to form the carbon dioxide radical anion, which is stabilized by hydration.[8] For the present experiments, hydrated carbon dioxide radical anions $CO_2^{\bullet-}(H_2O)_n$ ($n \approx 35$–75) are generated in a laser vaporization source and stored in the ion trap of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Upon collision with gaseous CH_3SH, a selective HAT is observed, with release of a radical of the composition $[C,H_3,S]^{\bullet}$ [reaction (1)]:

$$CH_3SH + CO_2^{\bullet-}(H_2O)_n \rightarrow HCO_2^{-}(H_2O)_{n-z} + [C,H_3,S]^{\bullet} + z\,H_2O \quad (1)$$

The kinetic analysis in Figure 1a indicates that the reaction proceeds with a rate $k_{abs} = (8.5 \pm 2.1) \times 10^{-10}\ cm^3\,s^{-1}$, close to the average dipole orientation (ADO) theory collision rate $k_{ADO} = 1.2 \times 10^{-9}\ cm^3\,s^{-1}$.[9] However, as a result of the considerable geometric cross section of water clusters, ADO as a pure ion-dipole capture theory underestimates the collision rate.[10] The true collision rate will lie between the hard-sphere ADO rate $k_{HSA} = 1.7 \times 10^{-9}\ cm^3\,s^{-1}$ and the surface charge capture rate $k_{SCC} = 3.3 \times 10^{-9}\ cm^3\,s^{-1}$.[10,11] This amounts to an efficiency of the reaction of 25–50%.

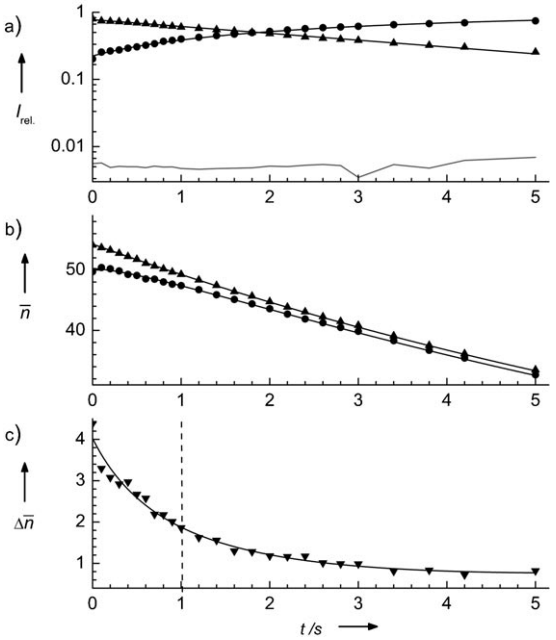

Figure 1. a) Pseudo-first-order kinetics for the reaction of $CO_2^{\bullet-}(H_2O)_n$ (▲) with CH_3SH to form $HCO_2^{\bullet-}(H_2O)_n$ (●). I_{rel} = relative intensity. b) Nanocalorimetric fit to the average cluster size $\bar{n}$. c) After 1 s, the difference in average cluster size $\Delta\bar{n}$ between reactant and product (▼) is fitted to minimize the influence of a possible drift in the initial cluster size distribution.

Visual inspection of the data in Figure 1b and c suggests that at least one water molecule evaporates as a result of the released reaction enthalpy. This is, however, an artifact of the experimentally required fill cycle of the ICR cell, which takes 2 seconds. Nanocalorimetric analysis with the help of recently derived differential equations[12,13] yields a value of $z = (-1.0 \pm 0.3)$ for the average number of evaporating H_2O molecules in reaction (1) (see Figure 1b and c). The result of the fit is extremely robust, and is repeatable for different data sets. A negative value of z implies an apparent growth of the cluster during the reaction. This fictitious growth intrinsically means that the newly formed product cluster is colder than the average reactant cluster. It needs additional heating

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before it starts to shrink again under the influence of blackbody radiation.[13]

To estimate the overall thermochemistry of the reaction and to learn more about the reaction mechanism, the reaction in small model systems was examined with quantum chemical calculations performed at the B3LYP/6-311++G** and M06X/6-311++G** levels of theory. Hydration energies of $CO_2^{\bullet-}$ and HCO_2^- converge in the $(H_2O)_n$ clusters with $n=3$–5 (see the Supporting Information, Figure S2). Thus, a cluster size of $n=5$ in reaction (1) is sufficiently large to model the immediate solvent environment of the molecular ions (see Figure 2). In the reactant $CO_2^{\bullet-}(H_2O)_5$ (**1**), the oxygen atoms of $CO_2^{\bullet-}$ are hydrogen-bonded to four water molecules, with hydrogen bond lengths of 2.01–2.02 Å, and the radical carbon center weakly interacts with one water molecule at a distance of 2.42 Å. In the HAT product $HCO_2^-(H_2O)_5$ (**2**), the hydrogen bonds between HCO_2^- and the water cluster are stronger, as evidenced by the shorter bond lengths of 1.88–1.94 Å. The C–H bond in **2** is pointing away from the water cluster.

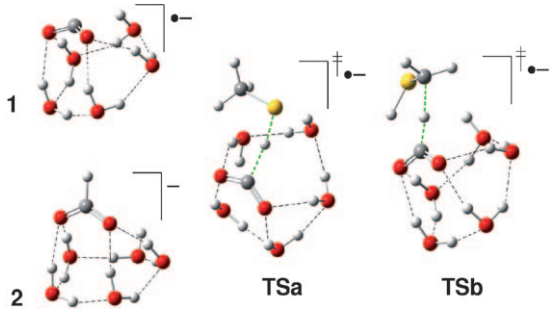
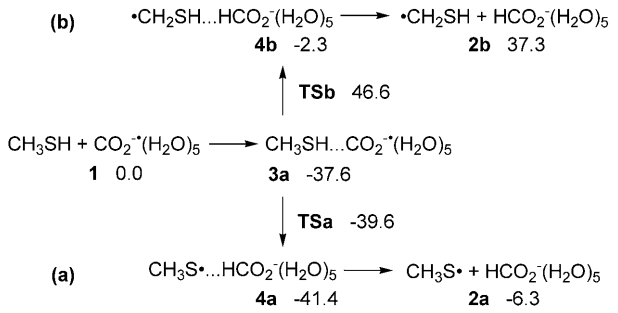


Figure 2. Optimized geometries of the reactant $CO_2^{\bullet-}(H_2O)_5$ (**1**) and the product $HCO_2^-(H_2O)_5$ (**2**) of reaction (1) with $n=5$. With CH_3SH as the reagent gas, **2** is formed via transition structures involving HATs either from the thiol (**TSa**) or the methyl (**TSb**) group. Dark gray C, light gray H, red O, yellow S.

With CH_3SH as the reagent gas, two reaction pathways are found which involve HATs from either a) the thiol group or b) the methyl group to the carbon center of $CO_2^{\bullet-}$ via the transition structures **TSa** and **TSb**, respectively (Figure 2). The reaction energies and mechanism are summarized in Scheme 1, and details are available as Supporting Information (Figure S3). Pathway a, HAT from the thiol group, proceeds barrierless. The binding energy of CH_3SH to **1** is -37.6 kJ mol^{-1}. The transition structure **TSa** was located on the potential energy surface featuring one imaginary frequency. Upon inclusion of zero-point correction, however, its relative energy is below the local minimum **3a**. This behavior is encountered quite frequently in hydrogen-transfer reactions,[14] where the high zero-point correction for X–H stretching modes changes dramatically from a local minimum structure with all intact bonds to the associated transition structure, in which one X–H mode becomes imaginary. The binding energy of the thiyl radical to $HCOO^-(H_2O)_5$ is -35.1 kJ mol^{-1}. The overall reaction is mildly exothermic by $\Delta H^\circ_0 = -6.3$ kJ mol^{-1}.



Scheme 1. Mechanism of reaction (1) with $n=5$. The relative energies with zero-point correction at 0 K (ΔH°_0 in kJ mol^{-1}) were evaluated at the M06X/6-311++G(d,p) level. Detailed energies and geometries are available in the Supporting Information.

Formation of the alternative thiomethyl radical $CH_2SH^\bullet$ via pathway b involves a critical transition structure **TSb** with a relatively high energy barrier of 46.6 kJ mol^{-1}. The separated products **2b** lie at 37.3 kJ mol^{-1}. The calculated energy difference between $^\bullet CH_2SH$ and $CH_3S^\bullet$ of 43.6 kJ mol^{-1} agrees within error limits with the experimental value of (38±9) kJ mol^{-1}.[15]

A HAT to an oxygen atom, which results in $HOCO^-(H_2O)_5 + CH_3S^\bullet$, was also examined. This reaction pathway is highly endothermic by 161 kJ mol^{-1}. The resulting HO–CO$^-$ bond is largely activated and easily breaks, forming $OH^-(H_2O)_5$ and CO with an overall reaction energy of 112 kJ mol^{-1}. While irrelevant for the present experiment, the instability of $HOCO^-$ may be responsible for CO poisoning in electrochemical cells,[5] or the intentional reduction of CO_2 to CO for energy storage purposes.[16]

The calculations unambiguously show that HAT proceeds through pathway a, since the intermediate **4a** with the thiyl radical bound to the product cluster is formed without barrier, while the alternative route b faces a significant barrier in **TSb**. For $n=5$, reaction (1) is calculated to be almost thermoneutral, whereas experiment suggests an endothermicity of $+(43\pm9)$ kJ mol^{-1}, the evaporation enthalpy of a water molecule,[17] for $n>30$. The discrepancy may result from the different cluster size regimes of experiment and calculation. If additional solvation stabilizes $CO_2^{\bullet-}$ more than $HCOO^-$, the energy of **1** is lowered relative to **2** with increasing cluster size. In this case, HAT from the thiol group becomes endothermic. More likely, however, is a dependence of the reaction cross section on the internal energy of the reactant cluster. If internally cold clusters react more efficiently than hot clusters, the product clusters will also be colder than expected. This scenario would fit a picture in which CH_3SH sticks to the cluster for an extended period of time before the thiol group finds the $CO_2^{\bullet-}$ radical. The residence time of unreacted CH_3SH in the cluster increases with decreasing internal energy. In this case, $z=-1$ means that only those clusters react that have evaporated an H_2O molecule shortly before the collision with CH_3SH. The above estimated reaction efficiency of 25–50% fits well into this picture.

In summary, $HCOO^-$ is formed selectively from CO_2 through a single electron transfer to CO_2, followed by a radical-type HAT from methyl mercaptan. This suggests that

thiol groups may improve the selectivity of electrocatalysts in sustainable electrochemical processes utilizing CO_2 as feedstock and water as solvent.

Experimental Section

Hydrated carbon dioxide radical anions $CO_2^{\bullet-}(H_2O)_n$ were generated in a laser vaporization source[18] and studied in a modified Bruker/Spectrospin CMS47X FT-ICR mass spectrometer.[13] Methyl mercaptan (Fluka, $\geq 99.0\,\%$) was introduced into the ICR cell by a needle valve at a constant backing pressure of $(9.2 \pm 2.3) \times 10^{-9}$ mbar. The progress of the reaction was monitored by measuring mass spectra after different delays relative to the end of the fill cycle of the cell. For kinetic and nanocalorimetric analysis, the total intensities of reactant and product clusters and the average cluster size were calculated, taking into account the contributions of the natural isotope distributions. Nanocalorimetric analysis and fits of experimental data were performed with a genetic algorithm as described previously.[13] Quantum chemical calculations at the B3LYP/6-311++G(d,p) and M06X/6-311++G(d,p) levels were performed with Gaussian 03[19] and Gaussian 09,[20] respectively. Refining the electronic energies obtained from the B3LYP level with a more accurate functional M06X had no qualitative effects on the overall thermodynamics and reaction mechanism, but the reaction enthalpy calculated from the latter was higher than that from the former for both reaction pathways a and b (see the Supporting Information, Figure S3).

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