

Spraying Water Microdroplets Containing 1,2,3-Triazole Converts Carbon Dioxide into Formic Acid

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Supporting Information

ABSTRACT: We report the use of 1,2,3-triazole (Tz)-containing water microdroplets for gas-phase carbon dioxide (CO₂) reduction at room temperature. Using a coaxial sonic spraying setup, the CO₂ can be efficiently captured by Tz and converted to formic acid (HCOOH; FA) at the gas–liquid interface (GLI). A mass spectrometer operated in negative ion mode monitors the capture of CO₂ to form the bicarbonate anion (HCO₃[−]) and conversion to form the formate anion (HCOO[−]). Varied FA species were successfully identified by MS/MS experiments including the formate monomer ([FA − H][−], *m/z* 45), the dimer ([2FA − H][−], *m/z* 91; [2FA + Na − 2H][−], *m/z* 113), the trimer ([3FA − H][−], *m/z* 137), and some other adducts (such as [FA − H + H₂CO₃][−], *m/z* 107; [2FA + Na − 2H + Tz][−], *m/z* 182). The reaction conditions were systematically optimized to make the maximum conversion yield reach over 80% with an FA concentration of approximately 71 ± 3.1 μM. The mechanism for the reaction is speculated to be that Tz donates the proton and the hydroxide (OH[−]) at the GLI, resulting in a stepwise yield of electrons to reduce gas-phase CO₂ to FA.

The transformation of carbon dioxide (CO₂) to formic acid has been extensively studied^{1–3} and is strongly motivated by two different factors, each of which is related to clean energy production. One of them is the possibility to capture carbon dioxide so that it is turned into useful small organic molecules that can be used as feedstocks and fuels, given that carbon dioxide levels in the atmosphere have started to exceed 400 ppm. Another is the possibility of creating a practical hydrogen storage system because formic acid (FA; HCOOH) has a volumetric hydrogen density of 53 g of H₂ per liter, which makes it a promising candidate. Formic acid is a valuable chemical commodity with a worldwide production of more than 800 kilotons per year.⁴ It is known that formic acid can be formed from carbon dioxide in different ways that involve the use of metal catalysts, electrochemistry, or photochemistry. In sharp contrast, the present work explores the possibility for the direct production of formic acid from carbon dioxide gas in contact with room temperature water microdroplets containing dissolved 1,2,3-triazole (Tz; C₂N₃H) as a catalyst. It is well-known that the rates of chemical reactions in microdroplets can be dramatically accelerated compared to the bulk solution and even yield new products.⁵ We take advantage of these features to transform gas-phase carbon dioxide into formic acid.

Previous investigations have revealed that amines and nitrogen-containing aromatic heterocycles such as pyridine, imidazole, triazole, and tetrazole in porous materials have a high affinity for the capture of CO₂.^{6–11} In particular, the 1,2,3-triazole (Tz)-incorporated metal–organic framework (MOF) can remarkably enhance CO₂ uptake capacity.¹² Tz mainly serves as the ligand in the above-mentioned MOF materials. In this work, we present an alternative approach that directly uses Tz as the CO₂ absorber and as the source of the hydrogen atom in water microdroplets to capture and convert CO₂ to

formic acid, which represents the first product of CO₂ hydrogenation and can be a precursor of higher value-added products. We were motivated to make this study when previous work showed that pyridine (C₅H₅N) was able to capture CO₂.¹³ A simple sonic spray setup is sufficient to conduct this CO₂/FA conversion in the Tz/water microdroplets (Figure 1).

The HPLC grade water was sprayed with N₂ as the nebulizing gas. A stainless-steel chamber was used to connect

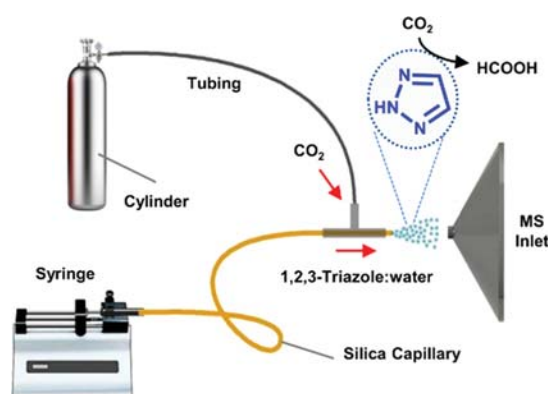


Figure 1. Diagram of sonic spray microdroplets monitored by a mass spectrometer.

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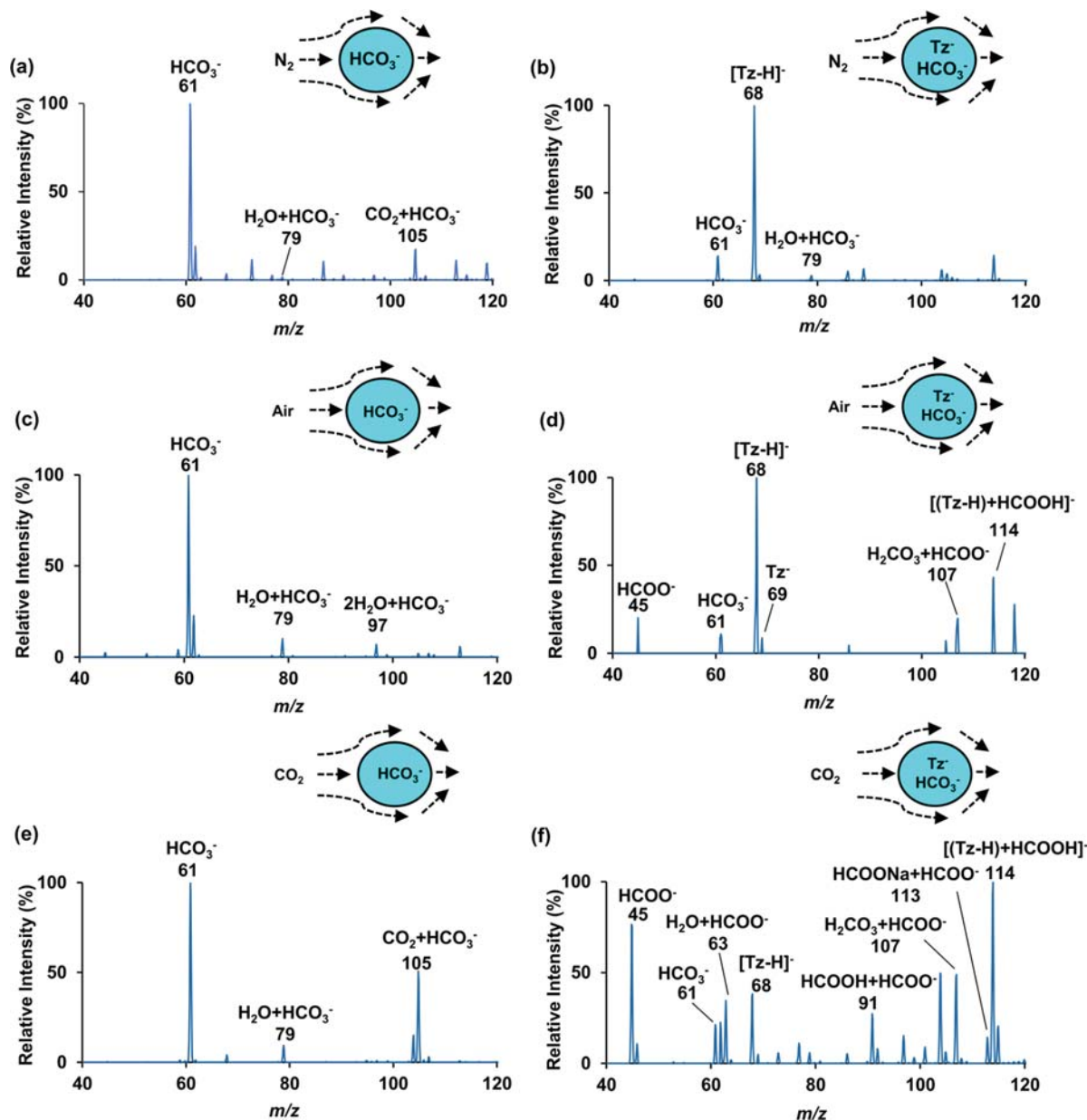


Figure 2. Mass spectra of sprayed microdroplets with different solutes and surrounding nebulizing gases: (a) water surrounded by N_2 ; (b) water containing Tz surrounded by N_2 ; (c) water surrounded by air; (d) water containing Tz surrounded by air; (e) water surrounded by CO_2 ; (f) water containing Tz surrounded by CO_2 .

the sonic spray tip and the mass spectrometer (MS) inlet to create a CO_2 -free environment (Figure S1). As a result, there were only carbonic acid-related peaks observed from the mass spectrum (Figure 2a) including bicarbonate ion (BC; HCO_3^- , m/z 61), hydrated ion ($[H_2O + HCO_3]^-$, m/z 79), and the CO_2 adduct ($[CO_2 + HCO_3]^-$, m/z 105). These peaks were all supposed to be generated from the CO_2 natively dissolved in water once exposed to the open air. Another negative control experiment was conducted by spiking Tz into the HPLC grade water and spraying it under the same conditions. No expected formic acid peak was detected by the mass spectrometer (Figure 2b). The formic acid peak was still not positively observed even when the HPLC grade water was replaced with carbonated water, which contains artificially injected CO_2 under high pressure (Figure S2). This result indicates that

CO_2 cannot be converted by Tz at the bulk phase or at the interior of a water microdroplet.

The stainless-steel chamber was removed to make the sprayed microdroplets contact gas-phase CO_2 in the air during the travel of the microdroplet to the MS. As a result, a set of FA-associated peaks (m/z 45 $[FA - H]^-$, m/z 107 $[(FA - H) + H_2CO_3]^-$, and m/z 114 $[(FA - H) + Tz]^-$) can be observed from the mass spectrum acquired from the Tz/water microdroplet group compared to that from the water group (Figure 2c,d). These results indicate that the Tz/water microdroplets effectively convert CO_2 into FA. In the previous negative control experiment, the Tz/water solution failed to convert the predissolved CO_2 into FA. On the basis of these findings, we initially proposed that the CO_2 /FA conversion occurred within the gas-liquid interface (GLI) region of the microdroplets. To validate this hypothesis, CO_2 was used to

replace N_2 as the nebulizing gas. As shown in Figure 2e,f, the FA production (m/z 45) strongly increased whereas the BC ion (m/z 61) decreased. This result further supports the contention that CO_2 reduction by the Tz/water microdroplet mainly happens in the GLI region.

To make the CO_2 conversion yield reach the optimum value, some critical sonic spray conditions were systematically investigated, as described in Figure S3. To validate the identity of the FA-associated ions, MS/MS experiments were conducted to obtain the fragment ion and neutral loss (NL) information for all ions of interest through collision-induced dissociation (CID). The results are presented in Figure S4 and described more fully in the Supporting Information.

The reaction mechanism has not yet been definitively established, but in the Supporting Information, we present speculation about how CO_2 is converted into FA. When the 1H on the Tz molecule was replaced with a methyl group, the CO_2 reduction process was blocked. This evidence indicated that the 2H on the Tz molecule (or 1H on the Tz tautomer) is the proton donor for CO_2 reduction. In addition, the failure of 1,2,4-triazole to reduce CO_2 gave additional evidence that Tz has a more favorable “ $-N=N-NH$ ” structure to bind with CO_2 and form a five-member planar complex, which is stabilized by a tetrel bond and a hydrogen bond. This assumption is also in agreement with previous structural calculations on the azole- CO_2 complex.⁹

Furthermore, a free radical scavenger, (2,2,6,6-Tetramethylpiperidin-1-yl) oxyl (TEMPO), was employed in the spraying of Tz/water microdroplets to investigate the electron transfer process during the CO_2 reduction. As a result, the FA monomer ($\cdot COOH$), dimer radical ($\cdot COOH + HCOOH$), and hydroxyl radical ($\cdot OH$) were successfully captured in the form of ions at m/z 202 ($[TEMPO - COOH + H]^+$), m/z 248 ($[TEMPO - COOH + FA + H]^+$), and m/z 173 ($[TEMPO - OH]$), respectively (Figure 3a). A CID-MS/MS experiment further supported that $m/z = 248$ is captured by TEMPO of the FA radical (Figure 3b). Therefore, we suggest that a stepwise electron transfer to this Tz- CO_2 complex leads to the formation of the formate anion ($HCOO^-$, Figure S5). We have known that the CO_2 reduction by Tz/water exclusively occurs in the GLI region. A growing number of studies have reported that the special redox reaction happened across the GLI region.^{14–18} This may be attributed to the strong electric field across the GLI.^{19,20} In this study case, we even observed that the TEMPO was reduced by losing its oxyl group (m/z 142) or hydrogenated to form the ions at m/z 157 and 158 (Figure 3a). These results also proved the special redox environment of the GLI and its critical role in the CO_2 reduction.

In terms of the source of free electron, we speculate that it is derived from more than one source. Besides the most predominant source, the hydroxyl group (HO^-), it could also come from the Tz anion (Tz^-) and even hydride (H^-) in an energy-free way.²¹ In one experiment, we also observed the Tz radical anion (Tz^- ; m/z 69) with a relative abundance of 10% (Figure S6). So, we presume Tz may also be reduced by a single electron transferred from the hydroxyl ion or other anion across the GLI. Then, the Tz radical anion continues to yield the acquired electron for CO_2 to be captured by Tz.

The concentration of the produced FA was then quantitatively estimated under the optimal sonic spray conditions. A diluted series of FA standard solutions ($n = 3$ /each) were directly injected into the MS to create a

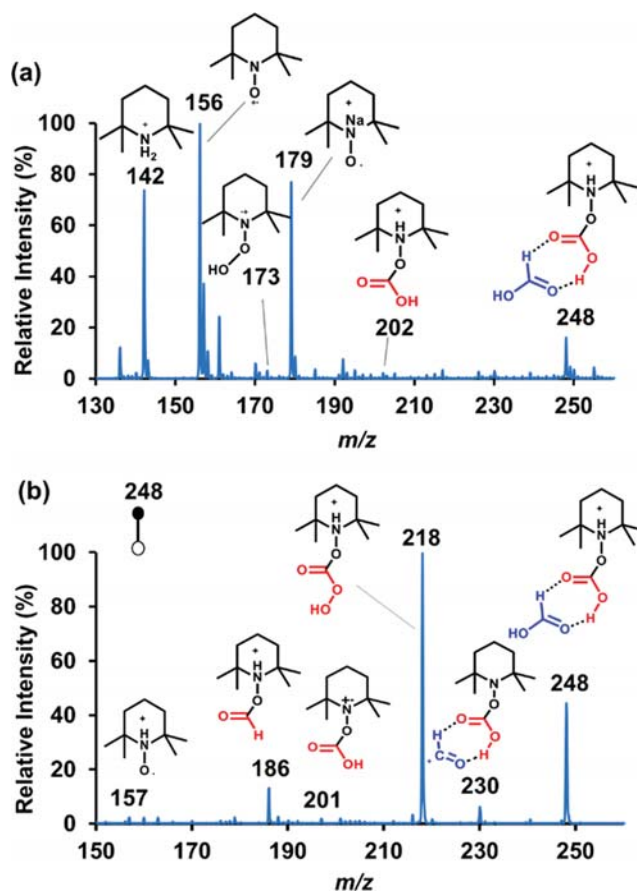


Figure 3. Characterization of the FA radical intermediate with the scavenger TEMPO. (a) The full scan mass spectrum of spraying Tz/water microdroplets containing TEMPO. (b) The identification of the precursor ion m/z 248 by an MS/MS experiment.

quantitation curve. Ion intensities of all FA-related ion species were summed up and normalized as the total response with their corresponding concentrations. Acetic acid ($[M - H]^-$, m/z 59) was used as the internal standard for normalization of the pH influence. Normalized FA intensity can maintain a linear relationship with the concentration from 2 to 200 μM (Figure 4a). Then, the total ion intensities of FA generated from different groups were compared against the quantitation curve to compute the concentration. The Tz/water microdroplets can achieve the highest FA production at $71 \pm 3.1 \mu M$ when they were sprayed while being surrounded by CO_2 . To give a relatively accurate estimation, we also took the neutral formic acid into account. On the basis of formic acid's pK_a of 3.75, the Tz/water solution pH at 5.5, and the estimated formate ($[HCOO^-]$) concentration of around 71 μM , the neutral formic acid is supposed to be $71 \mu M \times (10^{-5.5}/10^{-3.75}) = 1.3 \mu M$. It is also worth noting that there was a weak amount of FA detected in the water microdroplets (Figure 4b). This observation may indicate that the water microdroplet itself could also reduce CO_2 to FA due to its unique redox properties in the GLI region, possibly aided by dissolved trace impurities. Conversely, the system contains other isobaric species that have the same m/z value that contributes to the baseline intensity, leading to a high intercept of the calibration curve. However, its extent of CO_2 reduction was much lower than that converted by the Tz/water microdroplet. Tz serves as

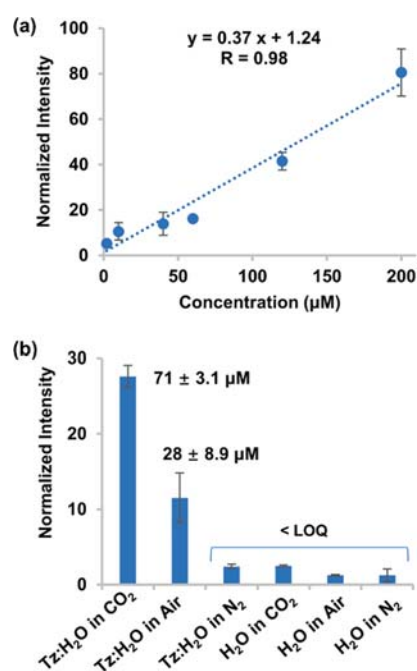


Figure 4. Quantitative estimation of formic acid produced by spraying Tz/water microdroplets at room temperature: (a) quantitation curve in which the error bars represent one standard deviation ($n = 3$); (b) formate anion signal strength for different conditions.

a more important means for CO₂ capture and conversion at the GLI.

After FA- and BC-related species identification, the carbon capture increment (ΔC) and conversion yield (Y) were calculated on the basis of the FA and BC intensities, as described in more detail in the [Supporting Information](#). Because FA and BC both exist in the microdroplets of various ionic species, the amounts of FA and BC were estimated by summing up each type of adduct ion intensity and neglecting the differences in ionization efficiencies. We find that the carbon capture increment was approximate 166.7%, meaning that spraying Tz/water microdroplets can capture 166.7% more carbon from the gas-phase CO₂ environment compared to that of pure water microdroplets ([Table S1](#)). It was also found that the sum of FA ion intensities was approximately 5-fold greater than that of the BC ions in the mass spectrum of sprayed Tz/water microdroplets. This result indicates that 84% of detected BC ions in the negative control group (pure water sprayed by CO₂ nebulizing gas) have been converted into FA by Tz (see [Figure S7](#)).

We have also roughly determined the turnover number, namely, how many CO₂ molecules are turned into FA per Tz molecule that is degraded. Assuming that we can recover Tz molecules complexed with FA, we estimated the turnover number is approximately 20 but the turnover frequency is extremely high (40 000 h⁻¹) because the reaction is completed within 300 μ s, given the speed of the spraying microdroplet of 80 m/s and a traveling distance of 24 mm. This turnover value is not as large as we might wish, and efforts are needed to determine whether some chemical modification of Tz or our operating conditions can produce a higher turnover number. Nevertheless, the production of FA from CO₂ with room temperature water without the application of any voltage seems to represent a new type of chemistry for this conversion process.

In summary, we have taken advantage of the special properties of water droplets, which have a much higher gas–liquid contact surface compared to the same volume in the bulk phase. By this means, we have demonstrated that Tz in sprayed water microdroplets can effectively capture gas-phase carbon dioxide in the liquid phase and further convert it into formic acid. It is confirmed that the CO₂ reduction predominantly happens at the gas–water interface of the microdroplet. The ultrafast conversion and high yield of formic acid suggest that Tz/water microdroplets might have potential as a CO₂ scavenger and as a new way to form formic acid, but more work is required to determine whether this procedure can offer practical advantages.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c07779>.

Identification of formic acid-associated ions; estimation of converted CO₂ fraction, carbon capture increment, and CO₂ conversion yield, turnover number, and turnover frequency; optimization of the sonic spray setup; the mechanism of CO₂ capture and reduction; photo of the stainless steel chamber; mass spectra; tuning of the sonic spray setup; quantitative identification of formic acid species; the possible mechanism of CO₂ capture and FA formation; monitoring of Tz ([PDF](#))

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Notes

The authors declare no competing financial interest.

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