

## Capturing Reactive Carbanions by Microdroplets

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**ABSTRACT:** Carbanions appear in many organic or biological reactions as fleeting intermediates, prohibiting direct observation or spectroscopic measurement. An aqueous environment is known to rapidly annihilate a carbanion species, reducing its lifetime to as short as picoseconds. We report that aqueous microdroplets can capture and stabilize reactive carbanion intermediates isolated from four classic organic reactions, aldol and Knoevenagel condensations, alkyne alkylation, and the Reimer–Tiemann reaction, enabling the detection of their carbanion intermediates by desorption electrospray ionization mass spectrometry. This is accomplished in real time of the reaction, allowing new insights into reaction mechanisms to be obtained. The efficacy of microdroplets in capturing such elusive species was examined by varying the solvent and the microdroplet negative charge density. We observed that microdroplets composed of water–methanol outperform other solvents, such as pure water, in capturing carbanions, which is in contrast to the earlier report that presented the highest performance of pure water microdroplets in capturing carbocations. We offer some mechanistic insights to explain the discriminatory behavior of these two oppositely charged species in microdroplets.

Carbanions are a class of negatively charged organic compounds in which an electron is often located predominantly on a carbon atom. More than one hundred years ago, carbanions were first proposed as a reactive intermediate in the classic benzoin condensation.<sup>1,2</sup> Because of its high nucleophilicity and basicity, many carbanions are exceedingly reactive and remain sparsely populated with a brief life in a reaction medium. Kinetics and laser flash photolysis experiments revealed that the average lifetime of such carbanions could be as short as  $10^{-11}$  s (Supplementary Note 1).<sup>3</sup> While the existence of persistent carbanions in organometallics or in the preparation of stable carbanion salts for nuclear magnetic resonance and mass spectrometric characterization is often described in the literature,<sup>4–11</sup> no general attempt was made so far to capture and isolate fleeting (metal-free) carbanion intermediate from a reaction medium for examining its time-dependent abundance. The lack of appropriate experimental probes may hide the actual reaction mechanism involving an elusive carbanion species in which some other plausible alternate mechanism is assumed to operate.<sup>12,13</sup> A recent report showed that the life expectancy of a carbanion intermediate generated by photolysis could be increased in dry zeolite by about 1 order of magnitude compared to that in the corresponding solution phase.<sup>14</sup> However, the study is limited to the convenient photochemical sources of carbanions (e.g., ketoprofen), which have a characteristic absorption band.

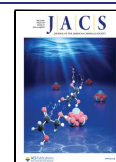
The present study shows that various types of intrinsically unstable carbanions can be successfully captured from different reactions using high-speed microdroplets containing water. The droplet evolution on a millisecond time scale<sup>15</sup> desorbs reactive (metal-free) carbanions to the gas phase for mass spectrometric detection, allowing real-time monitoring of the formation of such reactive species as intermediates. This work is influenced by our recent study that electrohydrodynamically

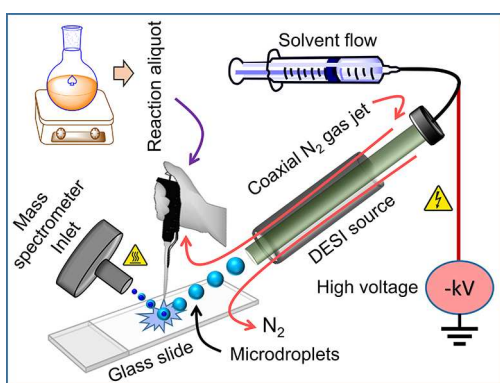
generated water microdroplets can intercept, stabilize, and transfer very effectively reactive carbocations from a reaction medium to the gas phase for mass spectrometric detection.<sup>16,17</sup> However, this report presents a strikingly different result: unlike carbocations, carbanions better survive in aqueous microdroplets containing methanol or acetonitrile. In addition to the carbanion stability in microdroplets, we also investigated the possible factors that may cause this difference.

Figure 1 illustrates our experimental workflow involving desorption electrospray ionization mass spectrometry (DESI-MS).<sup>18</sup> We investigated four classic reactions: aldol condensation, Knoevenagel condensation, alkylation of alkynes, and the Reimer–Tiemann reaction. These reactions are known to form various types of carbanion intermediates (enolates, acetylide anion, and trichloromethanide carbanion) as presented in Figure 2. Literature precedent indicates that the lifetime of such carbanion intermediates is very brief and might range from nanoseconds to picoseconds in solution (Supplementary Note 1).<sup>3,19–23</sup> We conducted these bulk reactions following protocols reported elsewhere (see the Supporting Information). We began our investigation by using negatively charged water microdroplets to bombard a small volume of a reaction aliquot (Figure 1) sampled at different time points during the reaction. This impact rapidly extracted the elusive carbanion species from the reaction aliquot into the splashed (secondary) microdroplets that evolved further to desorb the carbanion to the gas phase for mass spectrometric measurement. Figure 3 presents ion signals of different carbanion

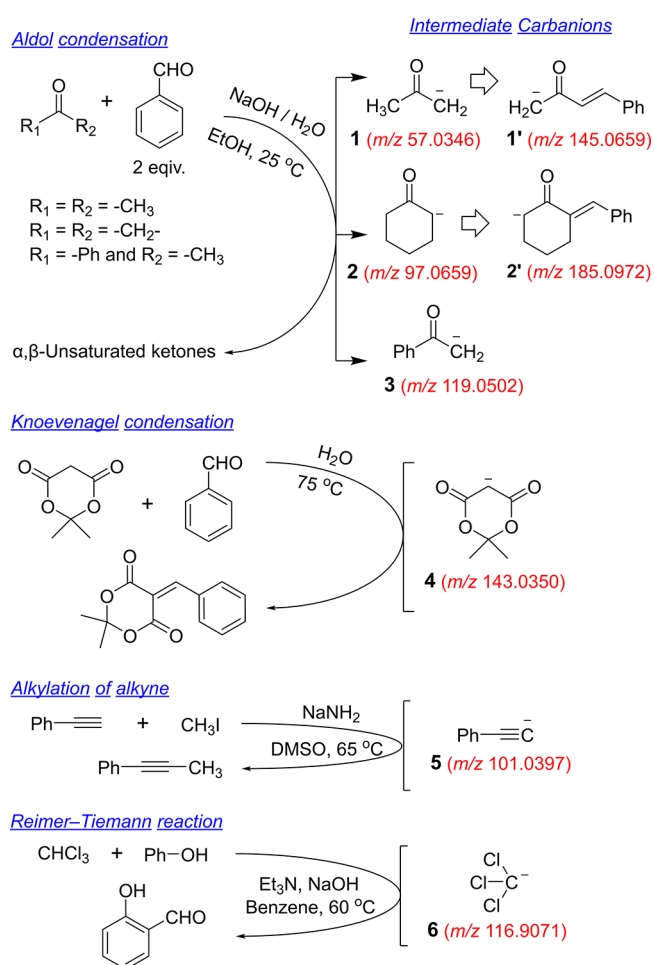
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**Figure 1.** DESI-MS experimental setup for capturing reactive carbanions on a millisecond time scale. A stream of microdroplets was allowed to bombard with 10  $\mu\text{L}$  of a reaction aliquot dispensed onto a glass slide. Chemical species from the aliquot were extracted in the splashed secondary microdroplets that further evolved, transferring the species to the gas phase (desolvation) for mass spectrometric detection.



**Figure 2.** Four classic reactions performed to generate reactive carbanions 1–6 as intermediates (Table S1). The theoretical  $m/z$  value of each carbanion is shown in red below its respective structure.

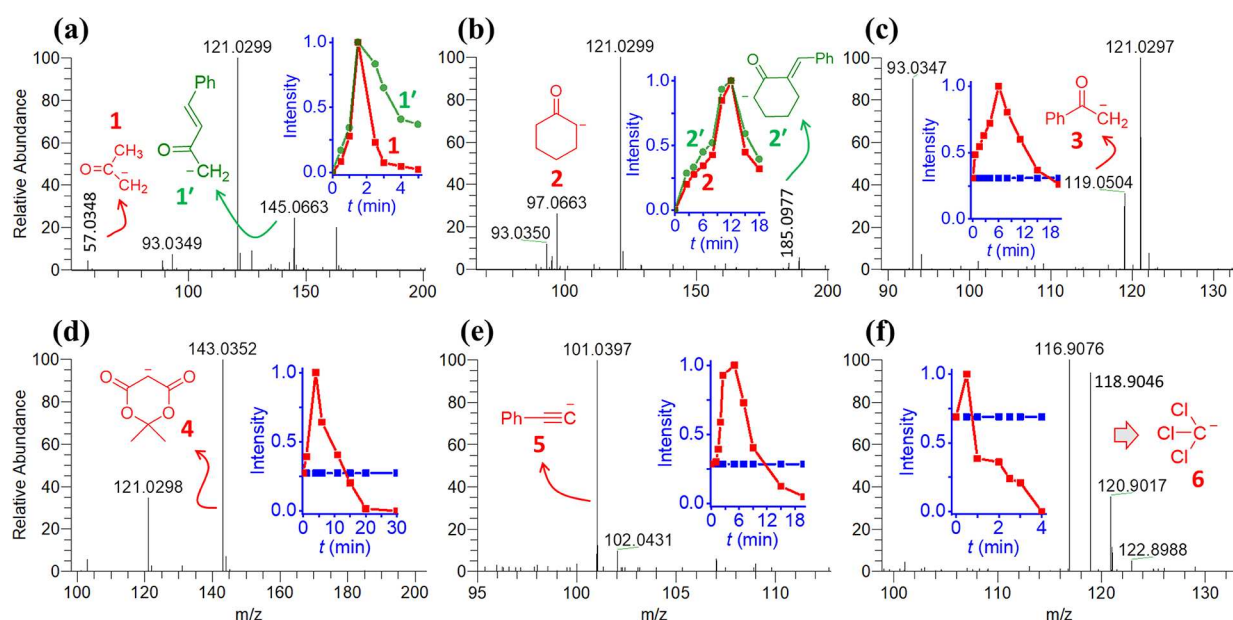
species captured from corresponding reactions in bulk (Figure 2) using aqueous microdroplets under the negative ion mode of DESI-MS (Figure S1). The high mass accuracy (Table S1) and resolution of the MS instrument accounted for the reliable identification of these fleeting intermediates, which were

further characterized by matching their simulated and experimental isotopic distribution patterns (Figure S2). The insets of Figure 3a–f present the temporal profiles of the corresponding carbanion abundance in each reaction (red and green curves).

These curves initially increase and reach a maximum at a certain age of the reaction, followed by a decrease as the reaction progresses further. This profile is in sharp contrast to the control study (without base and heat), where a less intense carbanion signal, wherever observed, remained constant throughout the course of the reaction (blue lines in insets of Figure 3c–f). This control result indicates that a partial contribution of negatively charged water microdroplets could deprotonate the substrate, but the intermediacy of the carbanion in the concerned reaction is supported by its hump-shaped plot of intensity vs reaction time as described above. Figures S3–S8 present the total ion current profile along with the mass spectrum of each individual reaction (Figure 2), indicating effective capture of the carbanion intermediate and related product immediately upon dispensing the reaction aliquot to the DESI source. It should be noted that the DESI-MS investigation of the reactions involving benzaldehyde found interfering signals of deprotonated benzoic acid ( $m/z$  121.029) and phenol ( $m/z$  93.035) (Figure 3a–d). These species are known to be generated by the oxidation of benzaldehyde in microdroplets,<sup>24,25</sup> and we have also reconfirmed that in the present study (Figures S9 and S10).

In another set of studies, we screened microdroplets of different electrospray-friendly solvents<sup>26</sup> (Table S2) to investigate their carbanion capturing efficiencies. The results are presented as histograms in Figure 4a. We observed better performance of microdroplets composed of binary aqueous–organic solvents (water/methanol or water/acetonitrile) over water alone in intercepting carbanion intermediates. When we compared this result with our earlier report on carbocation interception using microdroplets,<sup>16</sup> we found that carbanions are less sensitive than carbocations to the microdroplet solvent. Carbocation intensity using water microdroplets was many times higher (10 to 1000) than that from other solvent droplets. In some instances, carbocations (e.g., *tert*-butyl carbocation) were only captured using the water droplet.<sup>16</sup> However, carbanions were not found to behave similarly in the present study. Among all microdroplets (Figure 4a), those generated from the methanol–water mixture (1:1, v/v) could moderately better desorb carbanions into the gas phase, indicating the importance of the volatile polar organic solvent (methanol) in aqueous microdroplets for capturing carbanions. Tuning the solvent (5–50  $\mu\text{L}/\text{min}$ ) and sheath gas (100–170 psi back pressure) flow rates in the DESI source also did not alter the above result (data not shown). When we tuned the spray voltage from 0 to  $-5$  kV, we noted the gradual increment of the carbanion signal, indicating the importance of droplet charging for effective desorption of carbanions from the droplet surface (Figure 4b).

The above observations collectively suggest that both microdroplet solvent and the extent of negative charging play essential roles in capturing and transferring reactive carbanions from an ongoing reaction to the gas phase. The analogous mechanistic model that we proposed earlier for carbocation interception using aqueous microdroplets can also be considered to interpret the present observations.<sup>16</sup>



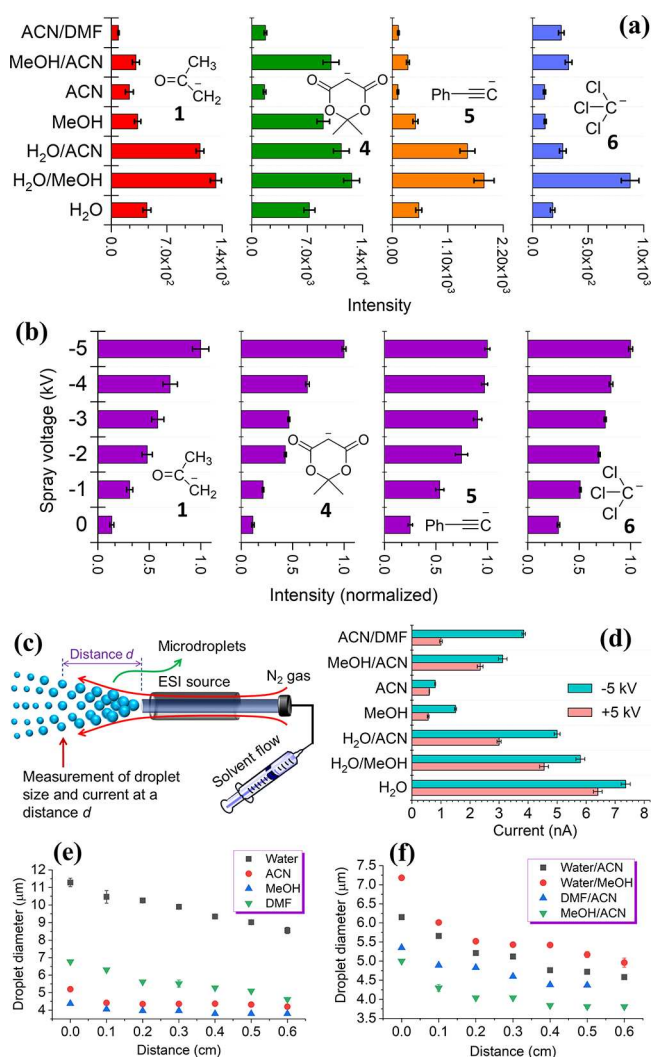
**Figure 3.** High-speed aqueous microdroplets in the DESI source (Figure 1) rapidly transferred the short-lived carbanions from the reaction aliquot (Figure 2) to the gas phase for mass spectrometric detection (a–f, Table S1). Insets present real-time monitoring of intermediate carbanion formation (intensity normalized to 1) with the progress of the reaction. The blue line presents the carbanion signal wherever observed from the control experiment (no base and heat applied, Figure 2).

The electrohydrodynamically generated microdroplets under negative potential accumulate hydroxide ( $\text{OH}^-$ ) ions from water reduction.<sup>26–28</sup> Unlike normal Brønsted bases, these  $\text{OH}^-$  ions lack their counter cations (acid), making the droplet overall negatively charged (vide infra) and a strong base. Carbanions extracted in such droplets should experience a considerably large Coulomb force of repulsion imparted by  $\text{OH}^-$  ions that reside at or nearer the droplet surface to minimize the potential energy.<sup>29–31</sup> The reactive carbanions ( $\text{R}^-$ ) possibly survive in such droplets by forming a tight ion pair in association with a counterion  $\text{M}^+$  (e.g.,  $\text{Na}^+$  from the reaction aliquot, see Figure 2)<sup>29</sup> inside the droplet or  $\text{R}^-$  might also exist on the charged surface to minimize the Coulomb repulsion. In the former case, when the tight ion pair ( $\text{R}^-\text{M}^+$ ) encounters the surface of the vanishing (evaporating) droplet, the surface hydroxide ions are thought to establish an attractive interaction with the counter cation ( $\text{M}^+$ ), facilitating the ejection of  $\text{R}^-$  from the surface by Coulomb repulsion. The carbanion may have the maximum life span and minimum reactivity on the droplet surface before desorption in the latter case. This is largely due to the vanishing water density at the air–water interface.<sup>32–36</sup>

It might be wondered why carbanions better desorb from a water–methanol droplet than a pure water droplet. This behavior contrasts to carbocations that showed highly efficient desorption from the water droplet.<sup>16</sup> To investigate the possible factors that affect this discriminatory behavior of the above two reactive species, we devised an experimental setup (Figure 4c, details in the Supporting Information) to measure currents emitted by droplets composed of different solvents (Figure 4d) and corresponding droplet evaporation profiles during flight (Figure 4e,f and Figure S11a–g). Figure 4d indicates that the overall net charge in droplets generated by a negative potential is higher than the positive potential of the same magnitude for all solvents under investigation. Although the exact reason for this phenomenon is currently uncertain, we are keen to investigate this further in the future. Figure 4e,f

suggests that the evaporation rate of water–methanol droplets is almost two times faster than that of water droplets within a 3 mm distance ( $d$ ) from the spray tip. However, the measured charge (current) is just 20% less in methanol–water droplets than in water droplets at the same distance ( $d = 3$  mm, Figure 4d). This indicates the increment of droplet charge density occurs at a much faster rate from methanol–water spray than water spray within a short flight (3 mm). We believe that this charge density alone does not facilitate ion ejection. Instead, the distribution of charges in microdroplets that creates an electric field from the droplet surface is important to consider. An earlier work using surface-sensitive vibrational sum-frequency generation spectroscopy revealed that the hydrated proton is orders of magnitude more surface active (attracted to the surface) than hydroxide at the water–air interface.<sup>37</sup> The study noted that protons affect the water surface at a few millimolar bulk concentration; on the contrary, the surface remains unperturbed until a several hundred millimolar hydroxide ion concentration. While the above report can be supported by some studies and contradicted by others,<sup>38–40</sup> it appears to be a trade-off between two important factors, e.g., droplet charge density and charge partitioning at the interface that guides the ion ejection in our study. The high surface affinity of protons (positive charges) generates a high electric field at the charged water droplet surface, effectively desorbing the carbocation species from the air–water interface.<sup>16</sup> In contrast, the hydroxide ion, having a relatively low surface affinity, rely more on its concentration (negative charge density) to affect the electric field at the droplet surface to facilitate the carbanion desorption. This is why, possibly, methanol–water microdroplets with high negative charge density outperform water microdroplets in capturing and detecting carbanions (Figure 4a). Likewise, the acetonitrile–water microdroplet also exhibited good efficacy in carbanion detection. However, on the basis of the trend of carbanion signals in Figure 4a, we do not rule out the possible role of other factors (solvent polarity, nucleophilicity, surface tension,





**Figure 4.** Screening of spray solvents, voltages, microdroplet charge, and sizes to elucidate the mechanism of carbanion capture. Four typical carbanions (1, 4, 5, and 6) were intercepted using different spray (a) solvents and (b) voltages. A schematic diagram of microdroplet spraying is presented in panel c to measure the (d) droplet current (absolute value) and (e, f) average droplet diameter (Figure S11a–g) derived from different spray solvents (insets). All data are presented as mean  $\pm$  SD from at least triplicate analysis.

etc.) in contributing to the capture of such reactive species. But the charge density and electric field at the droplet surface are likely to play dominant roles.

It should be noted that considering the lifetime of carbanion intermediates in the range of nanoseconds to picoseconds (Supplementary Note 1), the present study indicates the enhancement of carbanion lifetime by three to six orders of magnitude in a microdroplet that lasts for a few milliseconds.<sup>15</sup> Thus, this study offers a powerful direct observation tool for investigating reaction mechanisms involving elusive carbanion intermediate(s) (Supplementary Note 2).

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c01577>.

Supplementary Notes 1 and 2, materials and methods, DESI-MS data of each reaction, and isotopic distributions (PDF)

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### Notes

The authors declare no competing financial interest.

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