Designer “Quasi-Benzyne”: The Spontaneous Reduction of Ortho-Diiodotetrafluorobenzene on Water Microdroplets

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ABSTRACT: It has been widely shown that water microdroplets have a plethora of unique properties that are highly distinct from those of bulk water, among which an especially intriguing one is the strong reducing power as a result of the electrons spontaneously generated at the air–water interface. In this study, we take advantage of the reducing power of water microdroplets to reduce ortho-diiodotetrafluorobenzene (o-C$_6$F$_4$I$_2$) into a C$_6$F$_4$I$_2$••• radical anion. Photoelectron spectroscopy and density functional theory computations reveal that the excess electron in C$_6$F$_4$I$_2$••• radical anion. The C$_6$F$_4$I$_2$••• anion was further successfully utilized in a Diels–Alder reaction, a typical reaction for benzene. This study provides a good example of strategically utilizing the spontaneous properties of water microdroplets and generating an especially exotic anion, and we anticipate that microdroplet chemistry can be an avenue rich in opportunities for new catalyst-free organic reactions.

1. INTRODUCTION

Over the past few years, water microdroplet chemistry has emerged as a new paradigm of research for its exceptional ability to significantly accelerate chemical reactions by several orders of magnitude, outpacing the same reactions that occur in bulk water. What’s more remarkable is that microdroplets can sometimes trigger reactions that cannot occur in the bulk. It has been widely accepted that microdroplets accelerate chemical reactions via various mechanisms, including partial solvation, extreme pH conditions, and ultrahigh electric fields. Among these mechanisms, the spontaneous generation of an ultrahigh electric field on the surface of microdroplets is particularly fascinating. Such a high electric field at the microdroplet surface can even split the hydroxide ions (OH$^-$) in water into hydroxyl radicals (•OH) and electrons, making the microdroplets both oxidative and reductive. In this study, we focus on only the reducing power of microdroplets. Existing studies involve the reduction of pyridine into pyridyl anion, the reduction of chloroauric acid in aqueous solution into gold nanoparticles, and nanowires, the reduction of doubly charged viologens into singly charged radicals, the reduction of water into H$_2$, the reduction of transition metal ions, as well as the reduction of iodopentafluorobenzene to its parent anion radicals. A more comprehensive overview of the redox capabilities can be found in a literature review. The electric field on microdroplets could result from the alignment of the free O–H bonds of the interfacial water molecules. Other studies have proposed that the formation of electric double layers might cause the high electric field.

In this study, we extend the reducing ability of microdroplets to the ortho-diiodotetrafluorobenzene (C$_6$F$_4$I$_2$) molecule. The parent radical anion, C$_6$F$_4$I$_2$•••, was observed. This anion is exotic because the excess electron dwells on the I–C1–C2–I linkage, and it weakens both of the C–I bonds but strengthens the C1–C2 bond, making it resemble the benzene molecule (C$_6$H$_6$), which has a C1–C2 triple bond (vide infra). As a result, we name the C$_6$F$_4$I$_2$••• radical anion “quasi-benzyne”. This quasi-benzyne was further utilized in a Diels–Alder reaction, a typical reaction for benzene. This study provides a good example of strategically utilizing the spontaneous properties of water microdroplets and generating an especially exotic anion, and we anticipate that microdroplet chemistry can be an avenue rich in opportunities for new catalyst-free organic reactions.

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electric fields to catalyze DA reactions has also emerged as a new method.\(^{33-35}\) In this study, we achieved the DA reaction between the quasi-benzyne \(\text{C}_6\text{F}_4\text{I}_2^{**}\) and a furan-based diene in microdroplets, based on which we anticipate that microdroplet chemistry can provide a new pathway rich in opportunities for catalyst-free DA reactions.

### 2. RESULTS AND DISCUSSION

Detailed experimental methods are provided in the Supporting Information (SI). Figure 1a illustrates the setup of the microdroplet experiment in a glovebox filled with \(\text{N}_2\). The inlet of the mass spectrometer is inserted into the glovebox in an airtight manner for analysis purposes.\(^{36}\) A \(\text{C}_6\text{F}_4\text{I}_2\) aqueous solution was forced by a syringe pump through a fused silica capillary that sits inside a larger coaxial capillary through which high-pressure \(\text{N}_2\) sheath gas flows. The resulting spray of microdroplets is aligned with the inlet of the mass spectrometer operated in the negative mode of detection. The distance between the outlet of the sprayer and the mass spectrometer inlet is the flying distance of the microdroplets, which defines the microdroplet reaction time. Figure 1b presents a typical and clean mass spectrum of the \(\text{C}_6\text{F}_4\text{I}_2^{**}\)-parent anion at \(m/z = 402\). It originates from the spontaneous reduction of \(\text{C}_6\text{F}_4\text{I}_2\) by an electron, supporting the notion that electrons are readily available on microdroplets. The same experiment was carried out in the atmosphere, and the signal of \(\text{C}_6\text{F}_4\text{I}_2^{**}\) was notably lower than that in the glovebox, attributed to the oxidative nature of air.\(^{19}\) The collision-induced dissociation (CID) spectrum was used to confirm the structure of \(\text{C}_6\text{F}_4\text{I}_2^{**}\) (Figure S1).

In order to obtain insights into the geometric and electronic structures of \(\text{C}_6\text{F}_4\text{I}_2^{**}\), gas-phase photoelectron spectroscopy (PES) measurements and density functional theory (DFT) calculations were performed. A comprehensive description of the methods is in the SI. Briefly, a home-built apparatus combines a laser photoemission ion source, time-of-flight (TOF) mass spectrometry, and anion PES. We analyzed the kinetic energies of the resultant photoelectrons by crossing a mass-selected anion beam with a 266 nm laser beam. The energetics of the photodetachment process are governed by \(h\nu = \text{EBE} + \text{EKE}\), where \(h\nu\) is the photon energy, \(\text{EBE}\) is the electron binding (photodetachment transition) energy, and \(\text{EKE}\) is the electron kinetic energy. As illustrated in Figure 2a,

![Figure 1](image)

**Figure 1.** Spontaneous reduction of \(\text{C}_6\text{F}_4\text{I}_2\) in water microdroplets. (a) Experimental setup of the sprayer in a glovebox filled with pure \(\text{N}_2\). (b) Typical mass spectrum showing the spontaneous reduction products, \(\text{C}_6\text{F}_4\text{I}_2^{**}\).

![Figure 2](image)

**Figure 2.** Photoelectron spectroscopic and DFT studies of \(\text{C}_6\text{F}_4\text{I}_2^{**}\). (a) Spectra of \(\text{C}_6\text{F}_4\text{I}_2^{**}\) and \(I^{-}\). (b) Calculated structures of neutral and anionic \(\text{C}_6\text{F}_4\text{I}_2\). (c) Correlation diagram of the frontier orbitals of \(\text{C}_6\text{F}_4\text{I}_2^{**}\) from the combinations of two carbon sp\(^2\) orbitals and two iodine p orbitals. (d) Resemblance between the HOMOs of \(\text{C}_6\text{F}_4\text{I}_2^{**}\) and benzyne, and the NPA charges of \(\text{C}_6\text{F}_4\text{I}_2^{**}\).

<table>
<thead>
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<th>species</th>
<th>exp. EA</th>
<th>theo. EA</th>
<th>exp. VDE</th>
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<tr>
<td>(\text{C}_6\text{F}_4\text{I}_2^{**})</td>
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<td>1.77</td>
<td>2.84</td>
<td>3.01</td>
</tr>
<tr>
<td>(1/I^{-})</td>
<td>3.06</td>
<td>3.01</td>
<td>3.01</td>
<td>3.01</td>
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\(^{a}\)The calculations were performed at the B3LYP/aug-cc-pVTZ-(C,F,H,O)/aug-cc-pVTZ-PP(1) level of theory.
state of the neutral, which is also in good agreement with the calculated value, 4.42 eV. The spectrum of I in Figure 2a shows a sharp peak at 3.06 eV, corresponding to the well-known EA of iodine. The $\text{C}_6\text{F}_4\text{I}_2^{+*}$ spectrum obviously has features from I (red), which is a result of a two-photon process: the first photon dissociates $\text{C}_6\text{F}_4\text{I}_2^{+*}$ into $\text{C}_6\text{F}_4\text{I}$ and $\Gamma$, and the second photon photodetaches $\Gamma$. Figure 2b shows the calculated structures of $\text{C}_6\text{F}_4\text{I}_2^+$ and $\text{C}_6\text{F}_4\text{I}_2^{+*}$. The two C–I bonds are elongated from 2.11 Å in the neutral to 2.39 Å in the anion. This result is consistent with a previous study, where the $\text{C}_6\text{F}_4\text{I}_2^{+*}$ anion was generated and imaged by scanning tunneling microscopy. This large bond length change is also consistent with the observed wide EBE features from I. To further confirm the benzyne feature of $\text{C}_6\text{F}_4\text{I}_2^{+*}$, we designed a DA reaction between $\text{C}_6\text{F}_4\text{I}_2^{+*}$ and 5-methyl-2-furoic acid in microdroplets (Figure 3a). The furoic acid was chosen instead of furan because deprotonation of the carboxylic acid could facilitate the easy mass spectrometric detection of the products. The mixed solution of $\text{C}_6\text{F}_4\text{I}_2$ and 5-methyl-2-furoic acid was sprayed into microdroplets. The deprotonated product peak is at $m/z = 273$.

Here, we define the product percentage as $I(\text{Product-H})/\left[I(\text{Product-H}) + I(\text{C}_6\text{F}_4\text{I}_2^{+*})\right]$, where $I$ denotes the peak intensities. By adjusting the reaction distance from 5 to 60 mm, that is, to adjust the reaction time from 227 to 2727 μs, a clear increase of the product percentage was observed (Figure 3b), indicating that the airborne microdroplet, but not the gas phase inside the mass spectrometer, was where the reaction occurs. To investigate the significance of the air–water interface of the microdroplets, we also monitored the product intensity when the sheath gas pressure was changed (Figure 3c). An increase in the product percentage was observed upon consecutively increasing the pressure from 20 to 70 psi, and...
the product percentage exceeded 95% when the pressure reached 60 psi. Increasing the pressure decreases the sizes and increases the surface area to volume ratio of the droplets, demonstrating the importance of the air–water interface for the reaction. The mass spectra in Figures S2 and S3 support the trends presented in Figure Sb,c, respectively. DFT simulation of the reaction between C\textsubscript{6}F\textsubscript{4}I\textsubscript{2}\textsuperscript{−} and furan shows a reaction barrier of only 14.6 kcal/mol (Figure S4), further supporting the DA reaction of the “quasi-benzyne”.

3. CONCLUSIONS

To conclude, we have utilized the spontaneously generated electrons in water microdroplets to reduce C\textsubscript{6}F\textsubscript{4}I\textsubscript{2}\textsuperscript{−} into a C\textsubscript{6}F\textsubscript{4}I\textsubscript{2}\textsuperscript{−} radical anion, where the excess electron occupies the I−C1−C2−I bridge, which elongates the C−I bonds but shortens the C1−C2 bond. PES and DFT studies provided an atomic orbital level understanding of the unusual bond length change. Since the C1−C2 bond order in C\textsubscript{6}F\textsubscript{4}I\textsubscript{2}\textsuperscript{−} is higher than a double bond, it becomes similar to the benzene molecule, as a result, we name it a “quasi-benzyne”. The C\textsubscript{6}F\textsubscript{4}I\textsubscript{2}\textsuperscript{−} anion was further used for a DA reaction, a typical reaction for which the real benzene molecule is well known. This study has pushed the limit of the microdroplet’s ability of generating exotic anions via its reducing power. Since there are very few previous studies successfully applying furoic acid in reactions involving biomass valorization, we anticipate that microdroplet chemistry can be an avenue rich in opportunities for new catalyst-free DA reactions involving biomass valorization.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c02819.

Author Contributions
H.C., R.W., and T.C. contribute equally.

Notes
The authors declare no competing financial interest.

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REFERENCES