Gas-Phase Smiles Rearrangement of ortho-Nitro-substituted Diaryliodonium Cations and Their Mechanistic Insights

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Abstract

Rationale: Diaryliodonium salts are useful electrophilic reagents in organic chemistry, finding extensive applications in arylations and photo-induced polymerizations. However, the comprehensive mechanistic investigations, particularly concerning the mass spectrometric behaviors of diaryliodonium salts, are relatively scarce in the literatures. **Methods**: Diaryliodonium salts could be readily ionized in ESI-MS to give [Ar ^{1}-I $^{+}$-Ar ^{2}], and the high-resolution ESI-MS/MS experiments were conducted to investigate their gas-phase chemical reactions. **Results**: Investigations on ESI-MS/MS of [Ar ^{1}-I $^{+}$-Ar ^{2}] revealed two major fragmentation patterns: 1) Reductive elimination resulting the diaryl coupling product ion [Ar ^{1}-Ar ^{2}] $^{+*}$ by the loss of I. 2) Generating aryl cations [Ar ^{1}] $^{+}$ or [Ar ^{2}] $^{+}$ through cleavage of the C–I bonds. We unrevealed that the introduction of NO $_{2}$ into Ar ^{2} of [Ar ^{1}-I $^{+}$-Ar ^{2}] could lead to an unexpected fragmentation ion [Ar ^{1}O] $^{+}$ in MS/MS, arising from an O-atom transfer process from NO $_{2}$ to Ar ^{1}. Particularly, when NO $_{2}$ was *ortho*-positioned to the iodine in Ar ^{2}, the [Ar ^{1}O] $^{+}$ sometimes exhibited dominant behavior. **Conclusions**: Comprehensive ESI-MS/MS studies and theoretical calculations provided strong support for the O-atom transfer mechanistic pathway: [Ar ^{1}-I $^{+}$-(*o*-NO $_{2}$-Ar ^{2})] initially underwent a Smiles rearrangement to the intermediate [Ar ^{1}-O-(*o*-NO-Ar ^{2}I)] $^{+}$, which subsequently dissociated to [Ar ^{1}O] $^{+}$ or [*o*-NO-Ar ^{2}I] $^{+*}$. Herein, we proposed an unexpected " *ortho*-effect" in the gas-phase fragmentation reaction of [Ar ^{1}-I $^{+}$-(*o*-NO $_{2}$-Ar ^{2})], in which the crucial determinant factor for the aryl migration was identified as the Smiles rearrangement reaction.

Gas-Phase Smiles Rearrangement of *ortho*-Nitro-substituted Diaryliodonium Cations and Their Mechanistic Insights

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Methods : Diaryliodonium salts could be readily ionized in ESI-MS to give [Ar^1-I^+-Ar^2], and the high-resolution ESI-MS/MS experiments were conducted to investigate their gas-phase chemical reactions.

Results : Investigations on ESI-MS/MS of [Ar^1-I^+-Ar^2] revealed two major fragmentation patterns: 1) Reductive elimination resulting the diaryl coupling product ion $[Ar^1\text{-}Ar^2]^{+*}$ by the loss of I. 2) Generating aryl cations $[Ar^1]^+$ or $[Ar^2]^+$ through cleavage of the C–I bonds. We unrevealed that the introduction of NO_2into Ar^2 of [Ar^1-I^+-Ar^2] could lead to an unexpected fragmentation ion $[Ar^1O]^+$ in MS/MS, arising from an O-atom transfer process from NO_2 to Ar^1. Particularly, when NO_2 was*ortho* -positioned to the iodine in Ar^2, the $[Ar^1O]^+$ sometimes exhibited dominant behavior.

Conclusions : Comprehensive ESI-MS/MS studies and theoretical calculations provided strong support for the O-atom transfer mechanistic pathway: [Ar^1-I^+-(*o* -NO_2-Ar^2)] initially underwent a Smiles rearrangement to the intermediate [Ar^1-O-(*o* -NO-Ar^2I)]$^+$, which subsequently dissociated to $[Ar^1O]^+$ or [*o* -NO-Ar^2I]$^{+*}$. Herein, we proposed an unexpected "*ortho* -effect" in the gas-phase fragmentation reaction of [Ar^1-I^+-(*o* -NO_2-Ar^2)], in which the crucial determinant factor for the aryl migration was identified as the Smiles rearrangement reaction.

Key Words: Smiles Rearrangement, Nitro-substituted Diaryliodonium salts, ESI-MS/MS, O-atom transfer reaction

1 Introduction

Hypervalent iodine compounds (HICs) possess remarkable advantageous characteristics, including facile synthesis, low toxicity, and environmental friendliness, making them versatile tools in a wide range of organic reactions, such as functionalizations, rearrangements, aryl-coupling and cyclization reactions.[1-3] The notable feature of HICs is its ability to exhibit similar reactivity to the transition metal reagents due to the changes in valence states, thereby providing cost-effective alternatives to expensive organometallic catalysts and toxic heavy metal-based oxidants.[4,5] Within this category of HICs, diaryliodonium salts, also referred to as diaryl-λ^3-iodines following IUPAC nomenclature,[6] stand out as a unique class of HICs renowned for their utility as highly electrophilic arylating reagents under mild reaction conditions.[7] Apart from their synthetic applications, diaryliodonium salts play a significant role in semiconductor photolithography. For instance, the bis(4-(1,1-dimethylethyl)phenyl)iodonium salt is a type of useful ionic photoacid generators (PAGs). Additionally, the aryliodonium salts find widespread usage in photo-redox catalysis and serve as cationic photo-initiators in polymerization reactions, contributing to the production of diverse materials such as adhesives, coatings, composites, dental materials.[8-11]

In 1983, Gross et al. pioneered the use of mass spectrometry to investigate the gas-phase reaction between benzene radical cations and alkyl iodides, leading to the proposal of the $C_9H_{13}I^+$intermediate.[12] Six years later, the same group described the six fragmentation processes involving iodonium radical cations.[13] In 1989, Busch et al. employed fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS) to provide further insights.[9,10] Then, in 1992, Busch group combined FAB with semi-empirical calculations to examine iodonium salts and pointed out that *ortho* -hindered iodonium salts lacked the rearrangement process.[11] In 1995, Sam et al. made significant contributions by employing electrospray ionization mass spectrometry to investigate the oxidation of PhIO in methanol.[14] In 1999, Ochiai et al. made a noteworthy discovery concerning the dimerization of iodine(III) reagents using FAB.[15] Additionally, Silva and colleagues conducted detailed studies on the disproportionation reaction of (diacetoxyiodo)benzene (DAIB) in acetonitrile and methanol by employing high-resolution ESI-MS/MS techniques.[16,17] Our group intercepted and characterized the transient reactive α-λ^3-iodine alkyl acetophenone intermediate using ESI-MS/MS, thus validating the reaction mechanism proposed by Ochiai.[18] Rissanen's group dedicated to explore the role of iodonium ions in supramolecular chemistry.[19-22] Niu et al. identified the photoproducts of bis(4-tert-butylphenyl)iodonium salts using GC-MS and proposed a mechanism for the photolytic reaction.[8]

The Smiles rearrangement is an intramolecular nucleophilic aromatic substitution, in which the aryl group transfers within an aromatic ring to an adjacent carbon atom.[23] It is becoming increasingly recognized that the gas-phase Smiles rearrangement is not confined to the classical five-membered ring transition state. For examples, both Wang and Pan proposed transition states of six-membered rings, supported by theoretical calculations.[24-28]Additionally, Pan's group highlighted that carbon monoxide (CO) could be eliminated through a three-membered ring transition state.[29] Concerning the extrusion of sulfur dioxide (SO_2), Lu and Irikura suggested that this process occurred through a five-membered ring transition state.[30,31] In this case, Li proposed a three-membered ring pathway.[32] Wu et al. proposed a Smiles rearrangement involving a four-membered ring, providing an explanation for the loss of formaldehyde (H_2CO) following this skeletal rearrangement.[33]

Scheme 1 Schematics illustrating. (**a**) Mass spectrometric behaviors of nitroarenes in EI-MS: *ortho* effect of*o* -nitrotoluene and rearrangement of nitrobenzene; (**b**) Our previous work: the gas-phase rearrangement reaction from [CF_3-I$^+$-Ph] to [$PhCF_3$]$^{+*}$ by loss of I; (**c**) This work: gas-phase reduction elimination of [Ar^1-I$^+$-Ar^2] to aryl coupling product ion of [Ar^1-Ar^2]$^{+*}$with loss of an iodine atom and the generation of O-atom transfer product ion [Ar^{1}O]$^+$ from [Ar^1-I$^+$-(*o* -NO_2-Ar^2)] in ESI-MS/MS.

The *ortho* effect and rearrangement of nitroarenes in EI-MS have previously been investigated (**Scheme 1a**),[34,35] and we have studied on gas-phase intramolecular aryltrifluoromethylation of phenyl(trifluoromethyl)iodonium cation via loss of an iodine atom (**Scheme 1b**).[36] However, our recent findings have unveiled that the introduction of NO_2 to diaryliodonium salts had introduced an entirely new dimension to the fragmentation patterns, resulting in the unexpected O-atom transfer product ion [Ar^{1}O]$^+$ from [Ar^1-I$^+$-(*o* -NO_2-Ar^2)] (**Scheme 1c**). Surprisingly, the exploration of the fragmentation patterns of nitro-substituted diaryliodonium cations was limited in the literature. Hence, we comprehensively investigated various diaryliodonium cations using high-resolution electrospray ionization tandem mass spectrometry (ESI-MS/MS) and provided mechanistic insights into the understanding of their gas-phase reactions through theoretical calculations. The research results would be beneficial for the research for the chemical and mass spectrometric studies of these diaryliodonium salts.

2 EXPERIMENTAL

2.1 Chemicals and Reagents

Methanol and dichloromethane (DCM) were purchased from Merck KGaA (Darmstadt, Germany). All of the samples were provided by Jianwei Han research group at East China University of Science and Technology, Shanghai. The preparation methods could be referred to relevant articles.[37-39] Some structures of the diaryliodonium salts (**M**) were given in **Scheme 2** , while the rest structures were shown in **Scheme S1** , and they were labeled for convenience as **1** to **54** . Salts **24** , **33**and **34** contained OTs$^-$ as counter anion, the rest diaryliodonium salts contained OTf$^-$ as counter anion. DCM was a suitable aprotic solvent for preparing the solution of diaryliodonium salts. In most cases, the diaryliodonium salts were dissolved in DCM to prepare the sample solution at concentration of 1˜10 μg/mL for mass spectrometric analysis.

Scheme 2 Chemical structures of some diaryliodonium salts (**1** ˜**16**) in this study, Mes = mesitylene.

2.2 Mass Spectrometry

The high-resolution ESI-MS and subsequent high-resolution ESI-MS/MS experiments were performed on a Q Exactive HF Orbitrap mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a standard ESI interface. Nitrogen was used as the sheath gas, auxiliary gas and collision gas. The basic ESI conditions were: spray voltage, 3500 V; capillary temperature, 275 °C; probe heater temperature, 300 °C; sheath gas flow rate, 35 arbitrary units; auxiliary gas flow rate, 10 arbitrary units; while the selected collision energy depended on the dissociation capability of the precursor ions. Data acquisition and analysis were carried out with the Xcalibur software package (version 4.2.47, Thermo Scientific).

3 RESULTS AND DISCUSSION

3.1 The general fragmentation patterns of diaryliodonium cations

Firstly, we studied some representative diaryliodonium salts (**1** ˜**4** , structures were shown in**Scheme 2**). These diaryliodonium salts could be easily ionized by loss of OTf^- to give diaryliodonium cations [**M** –OTf]$^+$ in the form of [Ar^1-I^+-Ar^2] and their ESI-MS/MS were shown in **Figure 1** . According to the previous reports and our studies of these spectra,[13,36,40] we proposed two major fragmentation patterns of [Ar^1-I^+-Ar^2] cations: 1) Reductive elimination[10-13,36] to give diaryl coupling product ions [Ar^1-Ar^2]$^{+*}$ by loss of an iodine atom, followed by the generation of further fragment ions from these species. Such gas-phase reductive elimination rearrangement reaction was similar to our previous finding of the process from [CF_3-I^+-Ph] at*m/z* 273 to [$PhCF_3$]$^{+*}$ at*m/z* 146 by loss of an iodine atom in ESI-MS/MS of [CF_3-I^+-Ph];[36]2) The C–I bond cleavage to produce aryl cations [Ar^1]$^+$ or [Ar^2]$^+$, which might further give [Ar^1+H_2O]$^+$ or [Ar^2+H_2O]$^+$ and [Ar^1+N_2]$^+$ or [Ar^2+N_2]$^+$ adduct ions,[41] along with their respective fragment ions. This type fragmentation has also be found in the in ESI-MS/MS of [CF_3-I^+-Ph], in which C–I bond cleavage of [CF_3-I^+-Ph] at*m/z* 273 gave rise to [Ph]$^+$ at *m/z* 77 or [PhI]$^{+*}$ at *m/z* 204 by loss of CF_3.[36]

Taking the MS/MS of [**1** –OTf]$^+$ as an illustrative example, we observed that the reductive elimination of [Ph-I^+-Ph] gave diaryl coupling product ion biphenyl^{+*} at *m/z* 154 rather than I^{+*} at *m/z* 127. This divergence could be attributed to the significantly higher ionization energy of iodine (10.45 eV) compared to biphenyl (8.16 eV).[42]Meanwhile, C–I bond cleavage of [Ph-I^+-Ph] produced [Ph]$^+$ at *m/z* 77, along with [Ph+H_2O]$^+$ at *m/z* 95 and [Ph+N_2]$^+$ at *m/z* 105. Notably, we did not observe the formation of [PhI]$^{+*}$ at *m/z* 204, which could be attributed to the higher ionization energy of PhI (8.72 eV) in comparison to the phenyl radical (8.32 eV).[42]Therefore, [Ar^1-I^+-Ar^2] predominantly formed diaryl coupling product ions and aryl cations in ESI-MS/MS. The two principal fragmentation pathways of [Ar^1-I^+-Ar^2] originating from diaryliodonium salts (**1** ˜**4**) were depicted in **Scheme 3** . The structural assignments for fragment ions were supported by accurate mass measurements (see in **Table S1** ˜**S3**).

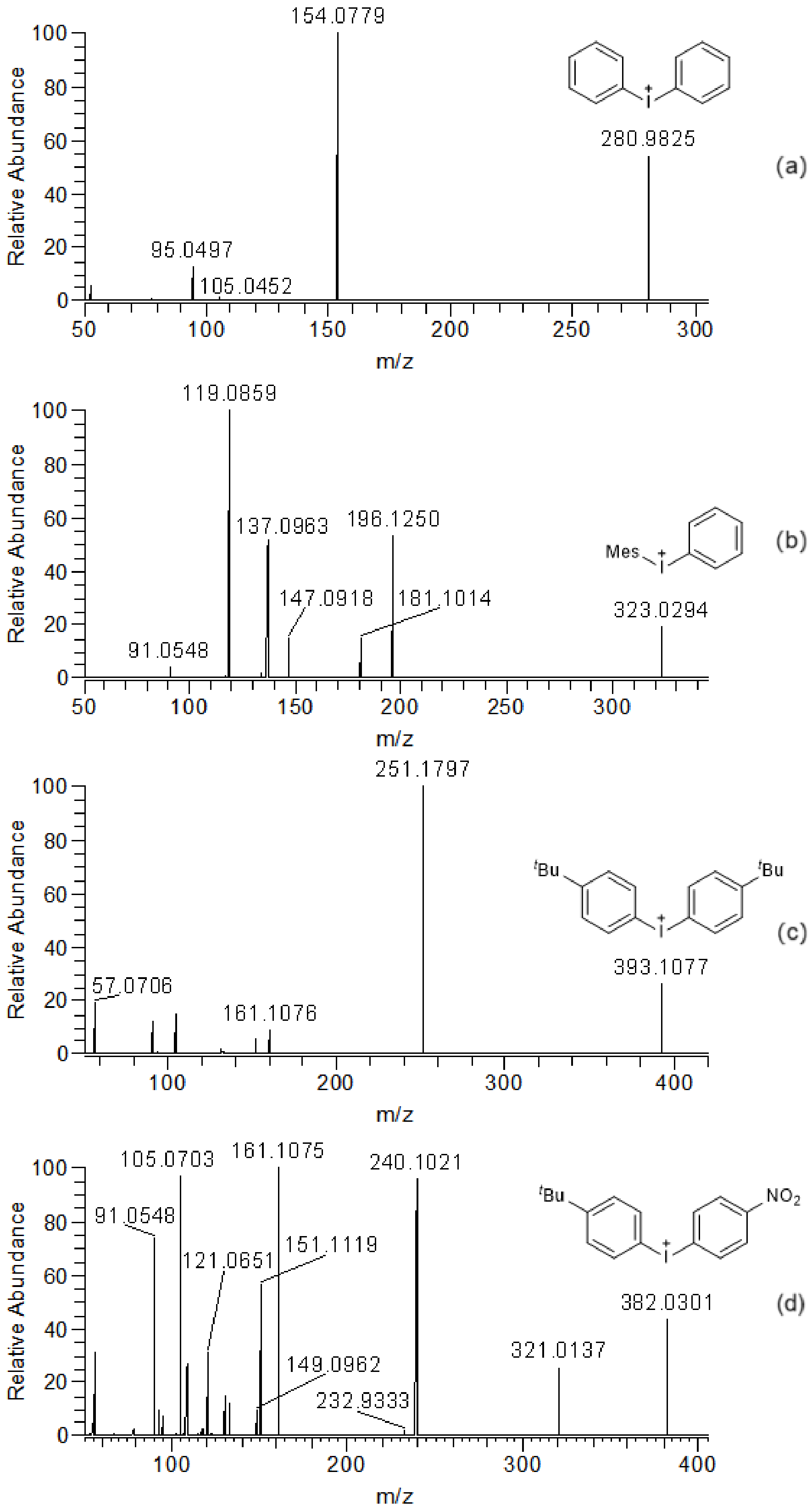
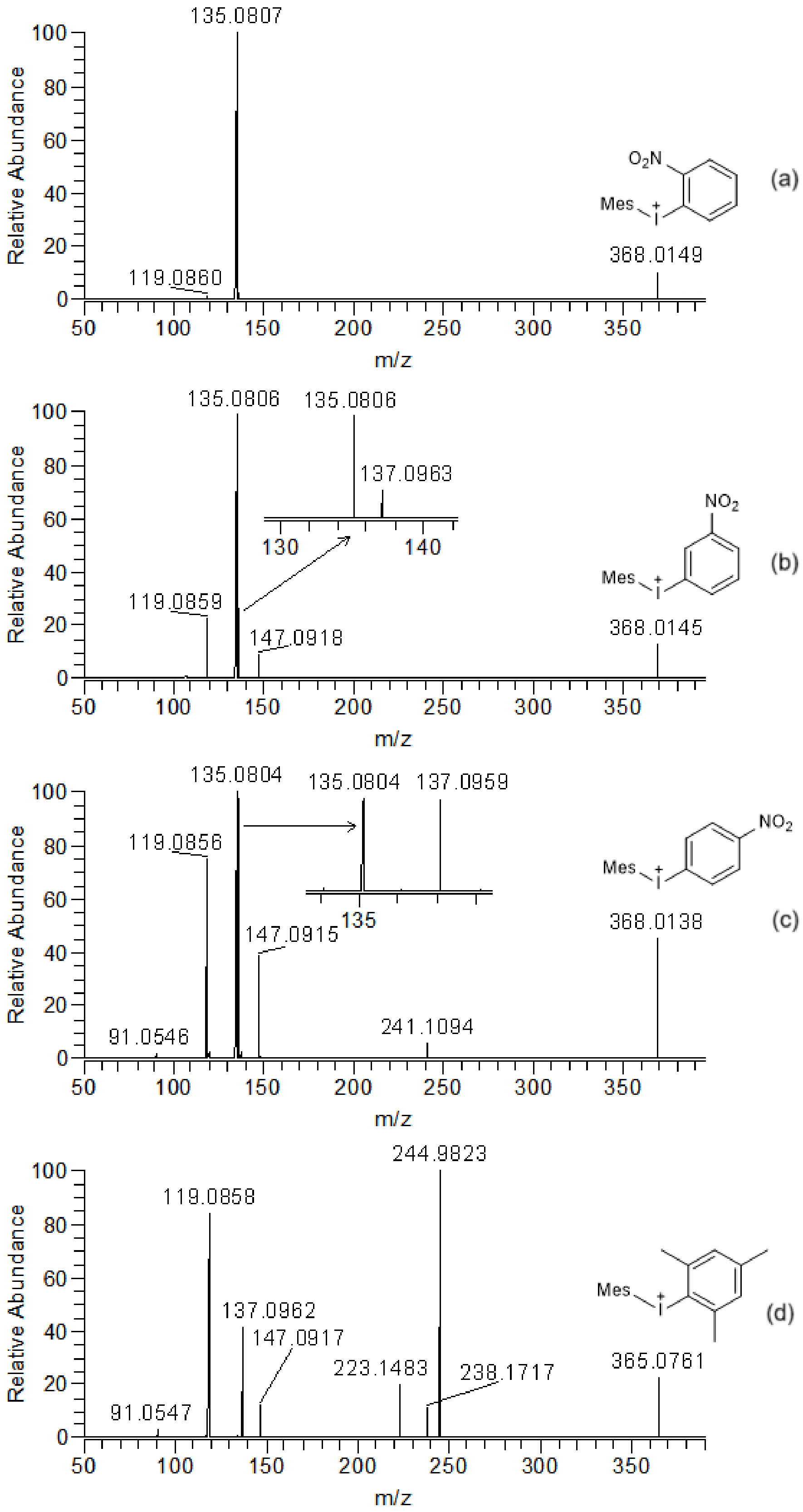

154.0779
280.9825
95.0497
105.0452
Relative Abundance
m/z
(a)
119.0859
137.0963
196.1250
147.0918
181.1014
323.0294
91.0548
Mes
(b)
251.1797
57.0706
161.1076
393.1077
^{t}Bu
(c)
105.0703
161.1075
240.1021
91.0548
121.0651
151.1119
149.0962
232.9333
321.0137
382.0301
NO_2
(d)

Figure 1 High-resolution ESI-MS/MS of [**M** –OTf]$^+$: (**a**) **1** , (**b**) **2** , (**c**) **3** and (**d**)**4** .

Scheme 3 Proposed fragmentation patterns of [**M** –OTf]$^+$: (**a**) **1** , (**b**) **2** , (**c**) **3** and (**d**)**4** .

When we examined diaryliodonium salt **4** with introduction of a nitro group into Ar^2, We not only observed fragment ions consistent with the processes outlined in **Scheme 3** but also identified novel types of fragment ions: [^{t} Bu-C_6H_4O]$^+$at *m/z* 149 and [*p* -NO-C_6H_4I]$^{+*}$at *m/z* 233 in the ESI-MS/MS of [(*p* -^{t} Bu-C_6H_4)-I$^+$-(*p* -NO_2-C_6H_4)] at *m/z* 382 (**Figure 1d** and **Scheme 3**). These findings strongly suggested the involvement of a gas-phase O-atom transfer reaction from the nitro group to the aryl moiety in the ESI-MS/MS of [(*p* -^{t} Bu-C_6H_4)-I$^+$-(*p* -NO_2-C_6H_4)]. It could be attributed to the presence of a nitro group in Ar^2 of the diaryliodonium cations.

3.2. Gas-phase rearrangements of nitro-substituted diaryliodonium cations



135.0807
119.0860
368.0149
O_2N
Mes
I⁺
(a)
135.0806
135.0806
137.0963
130
140
119.0859
147.0918
368.0145
NO_2
(b)
135.0804
135.0804
137.0959
135
119.0856
147.0915
91.0546
241.1094
368.0138
(c)
244.9823
119.0858
137.0962
147.0917
223.1483
238.1717
91.0547
365.0761
(d)
Relative Abundance
0
20
40
60
80
100
m/z
50
100
150
200
250
300
350

Figure 2 High-resolution ESI-MS/MS of [**M** –OTf]$^+$: (**a**) **5** , (**b**) **6** , (**c**) **7** and (**d**)**8** .

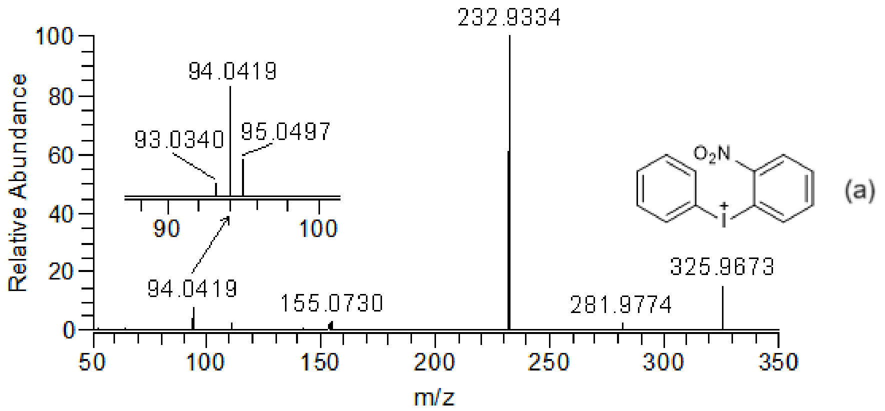
Scheme 4 Proposed rearrangement patterns of [**M** –OTf]$^+$ of salts**5** ~**7** .

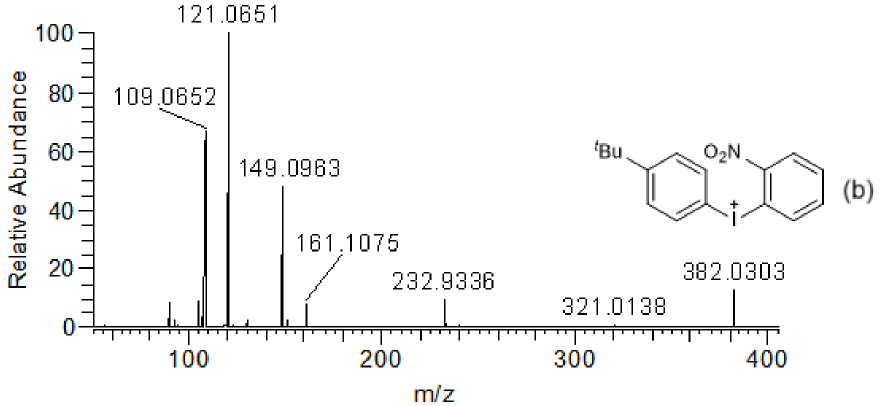
Based on the observation of O-atom transfer product ion [^{t} Bu-C_6H_4O]$^+$at *m/z* 149 from nitro-substituted diaryliodonium cation [**4** –OTf]$^+$, we extended to more diaryliodonium cations with salts **5** ~**7**as shown in **Scheme 1** , and the spectra of the salts**5** ~**7** with nitro substituent in different position (*ortho* , *meta* and *para*) of Ar^2 were depicted in **Figure 2a** ~**c** . To our delight, [Mes-I^+-(NO_2-C_6H_4)] from salts **5** ~**7** all exhibited the O-atom transfer product ion [MesO]$^+$ at*m* /*z* 135 with high abundances in their respective MS/MS. As a comparison, we also tested cations from salt **8** simultaneously (**Figure 2d**). However, the product ion [MesO]$^+$ at *m* /*z* 135 could not be observed in the MS/MS of [Mes-I^+-Mes] at*m/z* 365. The accurate mass measurements (in **Table S1** and**S2**) supported our explanations. These results collectively demonstrated that the introduction of a nitro group into Ar^2 of [Ar^1-I^+-Ar^2] could give rise to new type fragmentation ions [Ar^1O]$^+$ by O-atom transfer process from the nitro group in Ar^2 to Ar^1 in ESI-MS/MS of nitro-substituted diaryliodonium cations.

Most importantly, when the nitro group was in *ortho* -position of Ar^2, the fragmentation ion [MesO]$^+$ at *m* /*z* 135 dominated the tandem mass spectrum of [Mes-I^+-(*o* -NO_2- C_6H_4)] at *m* /*z* 368 from salt **5** , with only a minimal presence of [Mes]$^+$ at *m/z* 119 (**Figure 2a**). Two possible reaction pathways were proposed for the gas-phase O-atom transfer rearrangement of [**5** –OTf]$^+$ (**Scheme 4**):*path* (**a**) Smiles rearrangement via a six-membered ring transition state (TS **5a**) to intermediate **5b**[Mes-O-(*o* -NO-C_6H_4I)]$^+$, which finally dissociated to [MesO]$^+$ at*m* /*z* 135; *path* (**b**) Cleavage of the C–I bond to form another transition state (TS **5a**) and ion-neutral intermediate **5d** , which could directly give to [Mes]$^+$ at *m/z* 119 or further lead to intermediate **5b** and finally forming [MesO]$^+$ at *m* /*z* 135 (**Scheme 4**). Due to the distance problems, the [Mes-I^+-(*m* -NO_2-C_6H_4)] and [Mes-I^+-(*p* -NO_2-C_6H_4)] from salt **6** or **7** might follow a stepwise process involving ion-neutral intermediates [Mes$^+$ & (*m* -NO_2-C_6H_4I)] or [Mes$^+$ & (*p* -NO_2-C_6H_4I)] to generate the intermediate **6b**[Mes-O-(*m* -NO-C_6H_4I)]$^+$or **7b**[Mes-O-(*p* -NO-C_6H_4I)]$^+$, respectively. These intermediates ultimately resulted in the O-atom transfer product ion [MesO]$^+$ at *m* /*z*135 (here Ar^1 = Mes) with loss of neutral species [*m* -NO-C_6H_4I] or [*p* -NO-C_6H_4I] (**Scheme 4**).

3.3 Gas-Phase Smiles Rearrangement of *ortho*-nitro diaryliodonium cations

In order to clearly explain the gas-phase O-atom transfer reaction mechanism of [Mes-I^+-(*o* -NO_2-C_6H_4)] from salt **5** to the dominating fragment ion [MesO]$^+$, we further studied the tandem mass spectra of some [Ar^1-I^+-(*o* -NO_2-C_6H_4)] cations with different Ar^1 from salts**9** ~**12** (shown in **Scheme 1**) and these [Ar^1-I^+-(*o* -NO_2-C_6H_4)] cations all exhibited the oxygen-atom transfer product ions [Ar^1O]$^+$ by loss of neutral [*o* -NO-Ar^2I] (shown in **Figure 3**).


232.9334
94.0419
93.0340
95.0497
90
100
94.0419
155.0730
281.9774
325.9673
Relative Abundance
0
20
40
60
80
100
50
100
150
200
250
300
350
m/z
O_2N
I+
(a)


121.0651
109.0652
149.0963
161.1075
232.9336
321.0138
382.0303
Relative Abundance
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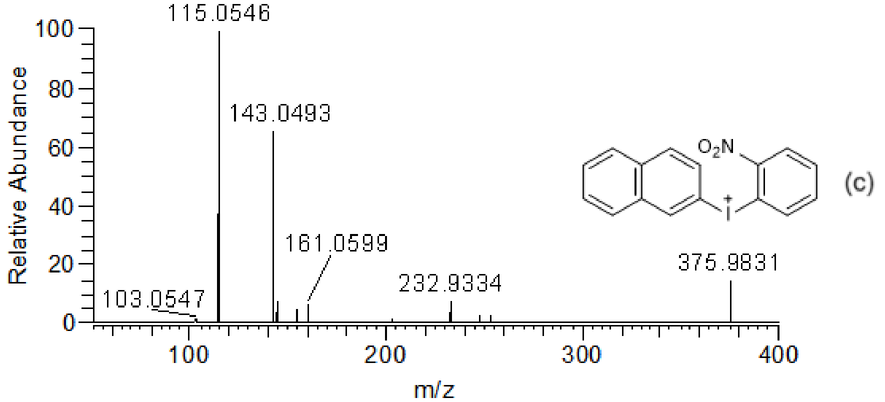
40
60
80
100
100
200
300
400
m/z
tBu
O_2N
I+
(b)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143.0493
161.0599
103.0547
232.9334
375.9831
Relative Abundance
0
20
40
60
80
100
100
200
300
400
m/z
O_2N
I+
(c)

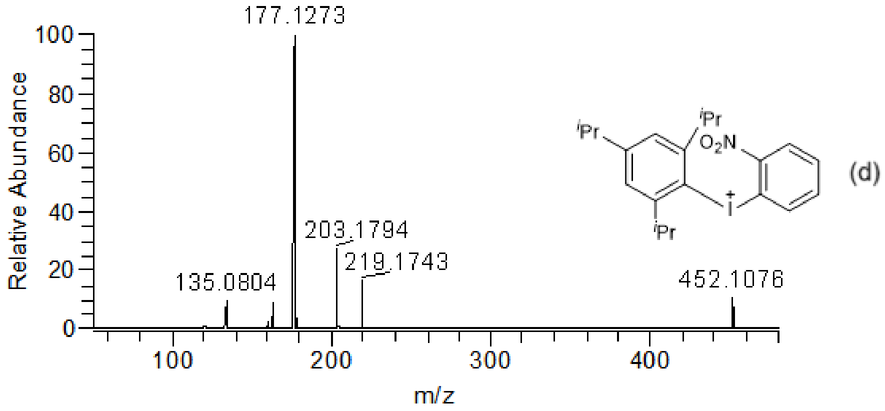
177.1273
203.1794
219.1743
135.0804
452.1076
Relative Abundance
0
20
40
60
80
100
100
200
300
400
m/z
iPr
iPr
iPr
O_2N
I+
(d)

Figure 3 High-resolution ESI-MS/MS of [**M** –OTf]$^+$: (**a**) **9** , the*inset* showed an expanded view of [PhO]$^+$ at*m /z* 93, (**b**) **10** , (**c**) **11**and (**d**) **12** .

To our surprise, the fragment ion [*o* -NO-C_6H_4I]$^{+*}$at *m /z* 233 appeared in the ESI-MS/MS of [C_6H_5-I$^+$-(*o* -NO_2-C_6H_4)] at *m/z* 326 from salt **9** . Meanwhile, this same fragment ion [*o* -NO-C_6H_4I]$^{+*}$at *m /z* 233 was also observed in the ESI-MS/MS of [**10** –OTf]$^+$ and [**11** –OTf]$^+$ (**Figure 3**). The structural assignments for fragment ions were supported by accurate mass measurements (in **Table S1** and **S2**). The fragment ion [*o* -NO-Ar^{2}I]$^{+*}$ was proposed to be the counterpart product ion of gas-phase O-atom transfer reaction from nitro to Ar^1 due to the charge transfer between the neutral [*o* -NO-Ar^{2}I] with [Ar^{1}O]$^+$. All these result supposed that the O atom in the [Ar^{1}O]$^+$ originated from the nitro group of Ar^2 to Ar^1. Consequently, the fragment ions [^{t} Bu-C_6H_4O]$^+$at *m/z* 149 and [*o* -NO-C_6H_4I]$^{+*}$at *m/z* 233 in the MS/MS of [**4** –OTf]$^+$ at *m/z* 382 (**Figure 1d** and **Scheme 3**) could be attributed to the gas-phase O-atom transfer reaction from the nitro group in Ar^2 to Ar^1.

Scheme 5 Proposed rearrangement patterns of [**M** –OTf]$^+$ of salts**9** ˜**11** .

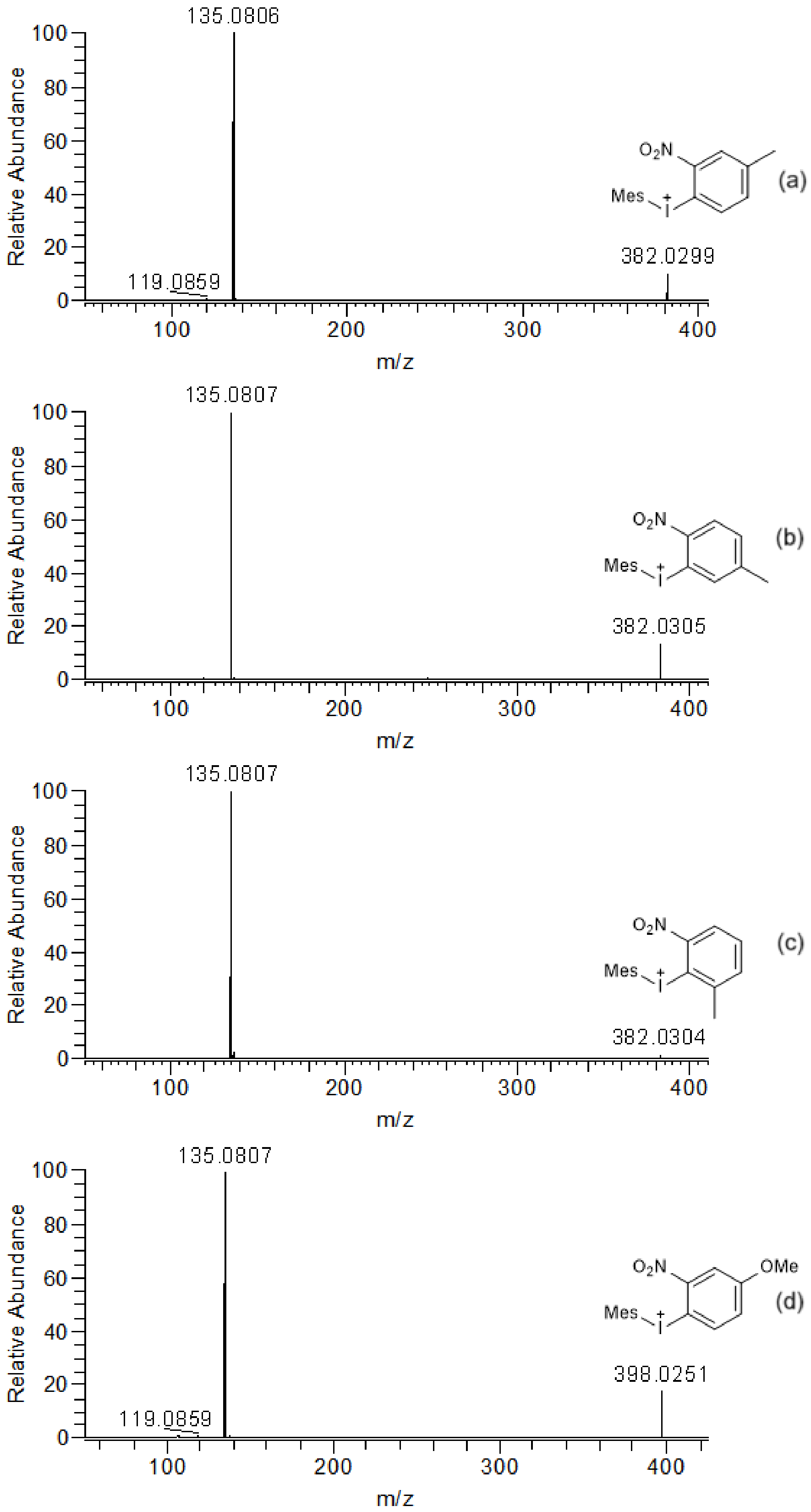
135.0806
119.0859
382.0299
O2N
Mes
I+
(a)
135.0807
382.0305
(b)
135.0807
382.0304
(c)
135.0807
119.0859
398.0251
OMe
(d)
Relative Abundance
0
20
40
60
80
100
m/z
100
200
300
400

Figure 4 High-resolution ESI-MS/MS of [**M** –OTf]$^+$: (**a**) **13** , (**b**) **14** , (**c**) **15** and (**d**)**16** .

However, the formation of product ions [Ar^{1}O]$^+$ from [Ar^1-I$^+$-(*o* -NO$_2$- Ar^2)] cations could not be simply rationalized by a one-step bond cleavage process. All the experimental results suggested that in the case of [Ar^1-I$^+$-(*o* -NO$_2$-Ar^2)], a Smiles rearrangement initially occurred, with the O-atom from the nitro group attacking the C$_{\text{(ipso)}}$ position of Ar^{1}I via a six-membered ring transition state, leading to the formation of the intermediate [Ar^1-O-(*o* -NO-Ar^{2}I)]$^+$. This transformation was accompanied by the reduction of the iodine (III) species to the corresponding iodine (I) species, which ultimately dissociated to produce [Ar^{1}O]$^+$(such as [MesO]$^+$ at *m /z* 135 in MS/MS of [**5** –OTf]$^+$, as shown in **Scheme 4** and Figure **2a**). This dissociation was achieved through the loss of neutral [*o* -NO-Ar^{2}I] or the generation of [*o* -NO-Ar^{2}I]$^{+*}$ by the loss of Ar^{1}O*. The ESI-MS/MS of [**M** –OTf]$^+$ (**M** =**13** ~**22** shown in **Figure 4a~d** and **S13** ~**S22**) exhibited striking similarity to the MS/MS of [**5** –OTf]$^+$, all prominently featuring [MesO]$^+$ at *m/z* 135 as the dominant fragment ion. Therefore, this unexpected "*ortho* effect" observed in the gas-phase fragmentation reaction of [Ar^1-I$^+$-(*o* -NO$_2$-Ar^2)] cations could likely be attributed to the Smiles rearrangement induced by the *ortho* effect of the nitro group.

3.4 Computations for gas phase rearrangements of nitro diaryliodonium cations

To shed insight to the reaction mechanisms of nitro diaryliodonium cations, density functional theory (DFT) calculations were performed with the Gaussian 16 package.[43] The geometries were fully optimized at the M062x/Def2-TZVP level in gas phase,[44,45] and harmonic vibration frequency calculations confirmed that the optimized structures were either minima (no imaginary vibrations) or transition states (only one imaginary vibration). The Gibbs free energies were given in kcal/mol and geometrical coordinates could be referred to the supporting information.

The schematic potential energy surface and the optimized structures of reactive species in ESI-MS/MS of [**5** –OTf]$^+$ resulting from the theoretical calculations were shown in **Figure 5** . Two paths of [**5** –OTf]$^+$ were considered, including*path* (**a**): the Smiles rearrangement via a six-membered ring transition state (**IAr2-*o*-TS1**); and *path*(**b**): the cleavage of the C–I bond to form another transition state (**IAr2-*o*-TS3**). The distance between C$_{\text{(ipso)}}$ and I, C$_{\text{(ipso)}}$ and O atom of nitro group in **IAr2-*o*-TS1** were 3.130 and 2.436 Å, which were both smaller than that of **IAr2-*o*-TS3** (4.367 and 4.589 Å, respectively). These results suggested that Smiles rearrangement of [**5** –OTf]$^+$ could facilely occur via a six-membered ring transition state (**IAr2-*o*-TS1**), leading to the formation of the intermediate **IAr2-*o*-INT1** .

Figure 5 Schematic of potential energy surface and the optimized structures of reactive species in ESI-MS/MS of [**5** –OTf]$^+$ (**IAr2-*o*-R**). The Gibbs free energies were given in kcal/mol.

The energy barrier for the Smiles rearrangement of *path*(**a**) via a six-membered ring transition state (**IAr2-*o*-TS1**) was only 22.7 kcal/mol and 9.5 kcal/mol less than the energy required for the C–I bond cleavage energy barrier of **IAr2-*o*-TS3** (36.0 kcal/mol). Furthermore, the Smiles rearrangement from the hypervalent iodine(III) complex**IAr2-*o*-R** to the iodane(I) intermediate**IAr2-*o*-INT1** (-14.9 kcal/mol) was exothermic, but the C–I bond cleavage to product complex **IAr2-*o*-INT3** (30.0 kcal/mol, which might give [Mes]$^+$ at *m/z*119) was endothermic. Thus, according to **Figure 5** , the Smiles rearrangement process of *path* (**a**) formed [Mes-I$^+$-(*o* -NO$_2$- C$_6$H$_4$)] (**IAr2-*o*-R**) to the intermediate [Ar^1-O-(*o* -NO-C$_6$H$_4$I)]$^+$(**IAr2-*o*-INT1**) via **IAr2-*o*-TS1** was a favorable reaction pathway both kinetically and thermodynamically. Then, the N–O bond cleavage of intermediate [Ar^1-O-(*o* -NO-C$_6$H$_4$I)]$^+$(**IAr2-*o*-INT1**) gave [MesO]$^+$ at*m /z* 135 by loss of neutral [*o* -NO-C$_6$H$_4$I] (**IAr2-*o*-INT2**) via transition state**IAr2-*o*-TS2** (energy barrier of only 12.4 kcal/mol). Such calculation results supported our hypothesis proposed for *path*(**a**) **IAr2-*o*-R** to intermediate**IAr2-*o*-INT1** via Smiles rearrangement and finally produced [MesO]$^+$ at *m /z* 135 with N–O bond cleavage of intermediate **IAr2-*o*-INT1** .

Meanwhile, the C–I bond cleavage to product complex**IAr2-*o*-INT3** (30.0 kcal/mol) might produce the intermediate **IAr2-*o*-INT4** (-10.2 kcal/mol) in *path*(**b**) and such process was exothermic. The N–O bond cleavage of intermediate **IAr2-*o*-INT4** might also give [MesO]$^+$ at *m /z* 135 and neutral [*o* -NO-C$_6$H$_4$I] (**IAr2-*o*-INT5**) via transition state**IAr2-*o*-TS4** (energy barrier of only 14.4 kcal/mol). The structures of the active species involved in the steps from**IAr2-*o*-INT3** to **IAr2-*o*-INT5** were same as those in the process from **IAr2-*o*-INT1** to**IAr2-*o*-INT2** , but the species with same structures had minor differences in relative energies due to the different spatial configurations in the finally optimized structures.

Figure 6 Schematic of potential energy surface and the optimized structures of reactive species in ESI-MS/MS of [**6** –OTf]$^+$ (**IAr2-*m*-R**). The Gibbs free energies were given in kcal/mol.

The *path* (**b**) of C–I bond cleavage process proposed for [**5** –OTf]$^+$ was unfavorable than Smiles rearrangement of *path* (**a**) (**Figure 5**). However, the Smiles rearrangement via O-attacking was not accessible for [**6** –OTf]$^+$ and [**7** –OTf]$^+$ due to their distances between $C_{(ipso)}$ and O atom of nitro group. Therefore, the stepwise processes involved ion-neutral complexes were considered for the explanation of the unexpected fragment ion [MesO]$^+$ at *m/z* 135 in ESI-MS/MS of [**6** –OTf]$^+$ and [**7** –OTf]$^+$. The schematic potential energy surface and the optimized structures of reactive species in MS/MS of [**6** –OTf]$^+$ and [**7** –OTf]$^+$ resulting from the theoretical calculations were shown in **Figure 6** and **7** . Theoretical calculations showed that [**6** –OTf]$^+$ and [**7** –OTf]$^+$ dissociated via similar mechanism as the *path* (**b**) of C–I bond cleavage process proposed for [**5** –OTf]$^+$, which was unfavorable than Smiles rearrangement of *path* (**a**) (**Figure 5**). However, the Smiles rearrangement via O-attacking was not accessible for [**6** –OTf]$^+$ and [**7** –OTf]$^+$, due to the fact that the distances between $C_{(ipso)}$ and O atom of nitro group in**IAr2-*m*-R** and **IAr2-*p*-R** were 4.783 and 7.265 Å, respectively, which were both much longer than that of**IAr2-*o*-R** (3.007 Å).

Figure 7 Schematic of potential energy surface and the optimized structures of reactive species in ESI-MS/MS of [**7** –OTf]$^+$ (**IAr2-*p*-R**). The Gibbs free energies were given in kcal/mol.

Therefore, the stepwise processes involved ion-neutral complexes were considered for explanation of the unexpected fragment ion [MesO]$^+$ at *m/z* 135 in ESI-MS/MS of [**6** –OTf]$^+$ and [**7** –OTf]$^+$. The energy barriers for the formation of **IAr2-*m*-TS1** and **IAr2-*p*-TS1**were 33.0 and 33.4 kcal/mol, respectively, which were both much higher than that of **IAr2-*o*-TS1** (22.7 kcal/mol). These results proved that the Smiles rearrangement process in**IAr2-*o*-TS1** was the most favorable path to give [MesO]$^+$ at *m /z* 135. Therefore, such calculation results explained why the fragmentation ion [MesO]$^+$ at *m /z* 135 dominated the MS/MS of [Mes-I$^+$-(*o* -NO$_2$- C$_6$H$_4$)] from diaryliodonium salts (**5** and**13** ~**16**) but only with tiny amount of [Mes]$^+$ at *m/z* 119.

To test the generality of the fragmentation patterns we proposed in this article, we further performed MS/MS experiments on cations from salts**17** ~**54** (structures shown in**Scheme S1**), and their tandem mass spectra and MS/MS data were summarized in **Figure S17** ~**S54** and**Table S1** ~**S4** . At the same time, pseudo-MS^3 experiments were performed in order to assign the origin of some ions (**Figure S55**~**S57**). These results showed the fragmentation ion [MesO]$^+$ from [**M** –OTf]$^+$ (**M** =**17** ~**22**) completely dominated the spectra (**Figure S17** ~**S22**) and diaryliodonium cations from salts**17** ~**36** also conformed well to the fragmentation patterns proposed in **Scheme 3** and **4** . The fragmentation patterns of cyclic diaryliodonium cations from salts**37** ~**54** were also characterized by loss of an iodine atom (**Scheme 6** , **Figure S37** ~**S54**).

Scheme 6 Proposed fragmentation patterns of [**M** –OTf]$^+$ from salts **37** ,**41** , **43** and **46** .

4 CONCLUSIONS

In summary, a total of 54 diaryliodonium cations were subjected to a comprehensive study using high-resolution ESI-MS/MS, and their fragmentation patterns were elucidated based on the accurate mass measurements of the resulting fragment ions. Our investigations unveiled that the incorporation of the nitro group into Ar^2 of [Ar^1-I$^+$-Ar^2] could lead to an unexpected type of fragment ion [Ar^{1}O]$^+$ through an O-atom transfer process from the nitro group to Ar^1 in their ESI-MS/MS. The particular case was the nitro group positioned in the*ortho* -position of Ar^2 moiety of the diaryliodonium salt. The theoretical calculations provided mechanistic insights into the O-atom transfer rearrangements of*ortho*- nitro-substituted diaryliodonium cations which supported the occurring of gas-phase Smiles rearrangement of [Ar^1-I$^+$-(*o* -NO$_2$-Ar^2)] to the intermediate [Ar^1-O-(*o* -NOAr^{2}I)]$^+$, finally giving the product ions [Ar^{1}O]$^+$ or [*o* -NO- Ar^{2}I]$^{+*}$. This work would be useful for the structural characterization of diaryliodonium cations by mass spectrometry, and the gas-phase Smiles rearrangement of [Ar^1-I^+-(o -NO_2-Ar^2)] might offer valuable insights for organic chemists for the design of new types of organic reactions involving diaryliodonium salts.

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CONFLICT OF INTEREST

There are no conflicts to declare.

AUTHOR CONTRIBUTIONS

Wu-Zhi Wei: Mass spectrometric investigations and writing draft. Cheng Pan: Compounds synthesis. Ling Lin: Theoretical calculations. Jianwei Han: Methodology, experiment designs, revising and editing. Hao-Yang Wang: Conceptualization, mechanism studies and supervision.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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