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Electrospray ionization multistage tandem mass spectrometry of penta- and hexa-substituted aryloxycyclotriphosphazenes

Zhiyu Ju[a,b], Yong Ye[a,c,*], Donghui Wei[a], Ruyi Zou[a], Yufen Zhao[a,c,*]

[a] Key Laboratory of Chemical Biology and Organic Chemistry of Henan Province, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, China
[b] College of Chemical and Chemical Engineering, Xunchang University, Xunchang 461000, China
[c] Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

Several penta- and hexa-substituted aryloxycyclotriphosphazenes were synthesized and investigated by electrospray ionization tandem mass spectrometry (ESI-MS^n). Their main fragmentation pathways are proposed based on the MS^n and accurate mass data. An apparent hydrolysis reaction is an important fragmentation process exhibited in the ESI-MS/MS spectra for all of them. Also interesting is the intramolecular electrocyclic ring closure observed in ESI-MS/MS spectra of them. These observations may have some potential applications in the distinction between the mass spectra of penta- and hexa-substituted hexachlorocyclotriphosphazene derivatives.

1. Introduction

Cyclophosphazenes are an important class of inorganic ring systems [1,2], not only because they have wide applications in biomaterials [3,4], thermosensitive materials [5], optical materials [6,7], electric photoconducting materials [8], advanced elastomeric [9], flame-retardant [10–13], rechargeable lithium batteries [14] and photostabilizing agents [15], but also because the reactions of various nucleophiles with the halogen atoms make it possible to modify the properties and applications of the phosphazenes to a great extent. However, most of the reported hexacyclotriphosphazene derivatives are hexa-substituted compounds, as an additive flame retardant, which leads to a great loss of mechanical properties for high polymers. Herein, we employ hexachlocyclotriphosphazenes to substitute partially with hydroxy aromatics, producing chloropentaaryloxycyclotriphosphazenes (**1**–**5** in Scheme 1), as reactive flame retardants.

Electrospray ionization multistage tandem mass spectrometry (ESI-MS^n) is a very powerful tool for structural determination and has been widely used in chemistry, flame-retardant mechanism, biochemistry and pharmaceutical research [16–20]. Although the electron ionization (EI) mass spectra of the thermal degradation products for aryloxycyclotriphosphazenes have been reported [21–24], the electrospray ionization (ESI) mass spectra fragmentation patterns of aryloxycyclotriphosphazenes have not been previously described. In this paper, we report the fragmentation patterns for penta- and hexa-substituted aryloxycyclotriphosphazenes obtained using ESI-MS combined with tandem techniques. And we discover that a hydrolysis is the most common fragmentation mechanism in ESI-MS/MS spectra of them. Besides this, it is exciting that a novel fragmentation mechanism, an intramolecular electrocyclic ring closure, is discovered in ESI-MS/MS spectra of penta- and hexa-substituted aryloxycyclotriphosphazenes.

2. Experimental

2.1. Chemicals syntheses

All compounds were synthesized according to the previous literature [25,26], and the structures were verified by FTIR, ^{31}P NMR, ^{1}H NMR, ^{13}C NMR, ESI-MS and accurate mass measurements.

2.2. Mass spectrometry

Mass spectra were acquired in the positive ion mode using a Bruker ESQUIRE 3000 ion trap spectrometer equipped with a gas nebulizer probe, capable of analyzing ions up to m/z 6000. Nitrogen was used as drying gas at a flow rate of 4.5 L/min. The nebulizer

* Corresponding authors at: Key Laboratory of Chemical Biology and Organic Chemistry of Henan Province, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, China. Tel.: +86 371 67767050; fax: +86 371 67767051.
E-mail addresses: yeyong03@tsinghua.org.cn (Y. Ye), jzy1696@163.com (Y. Zhao).

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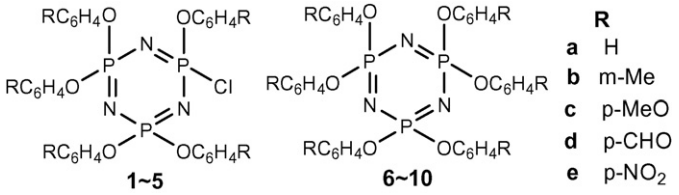


Scheme 1. Structures of **1**–**10**.

pressure was 7.5 psi. The capillary was typically held at 4 kV and the source temperature was maintained at 300 °C. The instrument was operated at unit-mass resolution, and calibration of *m*/*z* scale was performed using a standard ES-tuning-mix. The samples were continuously infused into the ESI chamber by a Cole-Parmer 74900 syringe pump (Cole Parmer Instrument Company, Vernon Hills, IL).

2.3. High-resolution mass spectrometry

The high-resolution mass spectral data for 1 was recorded on a Bruker APEXII Fourier transform ion cyclotron resonance (FTICR) MS instrument with an external ion source and analyzed using liquid secondary ion (LSI) MS with a Cs ion gun in the positive ion mode. The accelerating voltage of the ion gun was 10 kV and the acquisition range was from *m*/*z* 100 to *m*/*z* 600. The sample was introduced as methanolic solutions.

FTICR-MS data acquisition was controlled by XMASS. The software for automated data acquisition and processing has been described previously [27]. Here, an arbitrary limit of 5 ppm has been stipulated, if the sample measurement falls below this mass error then the measurement is accepted and the results returned to the chemist [28]. The robust nature of this approach has been proven since errors greater than 5 ppm for the correct formulas are not often encountered [28].

2.4. Computational details

To simplify the calculations, compound **1** was chosen as a model. All calculations were carried out at the B3LYP/6-31G(d,p) level using Gaussian 03W suite [29] of programs in the gas phase. A vibrational frequency calculation was then performed at the optimized geometry belonging to each reactant, product, transition state, and intermediate. We confirmed that all reactants and intermediates have no imaginary frequencies, and each transition state has one, and only one, imaginary frequency. The intrinsic reaction coordinate (IRC) calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products.

3. Results and discussion

As shown in Table 1, we observed that compounds **1**–**5** display similar fragmentation pathways (Scheme 2). In the ESI-MS^2 spectra of the protonated molecule $[M+H]^+$, the base peak is produced by loss of a RC_6H_4OH molecule to form the ion $[M+H-RC_6H_4OH]^+$ (assigned as ion A), which further fragments into ions $[M+H-2RC_6H_4OH]^+$, $[M+H-RC_6H_4OH+H_2O-RC_6H_4OH]^+$, $[M+H-RC_6H_4OH-18\ Da]^+$, $[M+H-RC_6H_4OH-HCl]^+$, $[M+H-RC_6H_4OH+H_2O-RC_6H_4OH-HCl]^+$ and $[M+H-2RC_6H_4OH-HCl]^+$ (assigned as ions A_a, A_b, A_c, A_d, A_e and A_f, respectively). Formation of these ions will be discussed in detail below. Another fragment ion $[M+H-HCl]^+$ (assigned as ion B) is formed by elimination of an HCl molecule.

First, we discuss the fragment ion A_a. Loss of another RC_6H_4OH molecule from the ion A might be interpreted as resulting from an intramolecular electrocyclic ring closure, as shown in Scheme 3. The formation of transition state TS1 involves a phosphonium ion attacking the *ortho*-position on the aromatic ring, assisted by an intramolecular hydrogen bond (C–H···N=P). The transition state TS1 converts into the ion M1 by cleavage of a carbon–hydrogen bond. The M1 then isomerizes to transition state TS2 by the formation of another intramolecular hydrogen bond (P=N–H···O). Subsequently a nitrogen–hydrogen bond in the ion TS2 is cleaved to yield the ion M2. Expulsion of a RC_6H_4OH molecule from the ion M2 finally yields the more stable ion A_a. It is known that the four-membered ring analogues were successfully synthesized by Heim et al. and Denney and Felton [30,31], which accounts for the feasibility of four-membered ring structure. Denney [24] believed the first step of the above mechanism must be assisted by the positive charge which acidifies the *ortho* protons on the aromatic ring. Namely, it is crucial that chemical reactivity of the *ortho* hydrogens be increased. And it is important that the proper base be employed to form hydrogen bonds or capture hydrogen atoms in order to increase its reactivity. Therefore, an intramolecular hydrogen bond (C–H···N=P) plays a critical role in the formation of the ion A_a.

In order to validate the formation mechanism of the intramolecular electrocyclic ring closure for the ion A_a, a theoretical calculation was carried out using the DFT method. All compounds shown in Scheme 3 will be subsequently referred to by their associated number in the interest of brevity. The corresponding representation of the potential energy profile is illustrated in Fig. 1. As is shown in Fig. 1, TS1 lies 32.96 kcal/mol above the energy of the reactant (A), whereas M1 lies 14.23 kcal/mol below that of the reactant (A), which indicates that it is a exothermic process and M1 is easily formed. Then M2 (+24.35 kcal/mol) has formed by M1 traversing the transition state TS2 (+35.38 kcal/mol). The M2 can easily decompose into the two products: A_a and a phenol molecule by phosphorus–oxygen bond cleavage. This means that our proposed mechanism is supported by the results of the theoretical calculation.

To certify the proposed structure of the ion A_a (using compound **1** as the example), the mass-to-charge ratios of the ions A and A_a at *m*/*z* 542.0358 ($[M+H-PhOH]^+$, $C_{24}H_{20}ClN_3O_4P_3^+$), and 447.9932 ($[M+H-2PhOH]^+$, $C_{18}H_{14}ClN_3O_3P_3^+$) were measured using the FTICR instrument (Table 2). The correlation between the measured and theoretical values (i.e., small error) supports the proposal for the A_a structure.

Next, the ion A_b most probably arises through a hydrolysis reaction where water attacks phosphorus cation, followed by elimination of a RC_6H_4OH molecule (Scheme 4). The proposed process begins with the attack of the water molecule at the phosphorus cation of the ion A. Then a hydrogen bond between the hydrogens on the water and oxygens on aryloxy group is formed to produce the ion TSA_b. Elimination of a RC_6H_4OH molecule from this ion sub-

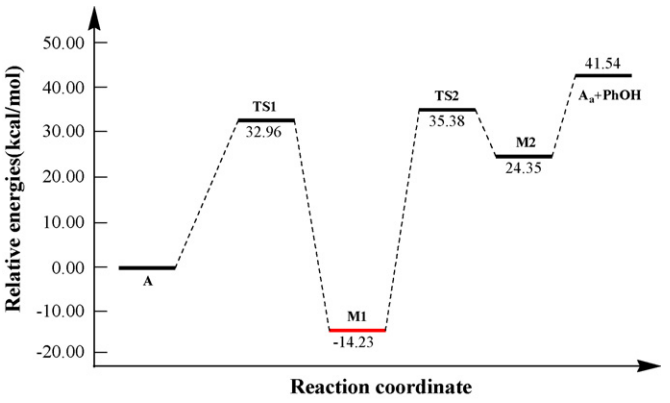


Fig. 1. Potential energy profiles for the whole reaction along the reaction coordinate for the compound **1**.

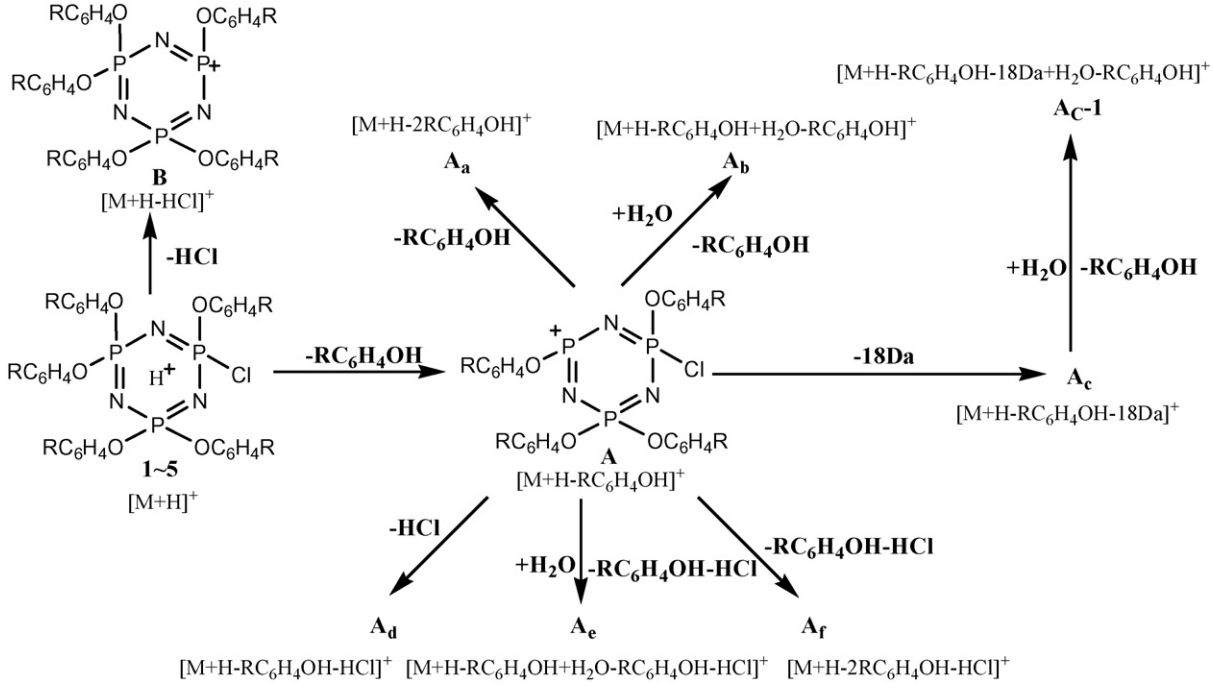
Table 1
ESI-MS^n data of the compounds **1**–**10** $[M+H]^+$.

Compds	Precursor ions, *m*/*z*	Fragment ions, *m*/*z* (relative abundance, %)								
		B	A	A_a	A_b	A_c	A_d	A_e	A_f	A_c-1
1	636(29) 542(68) 524(22)	600(11)	542(100)	448(34) 448(71)	466(39) 466(100)	524(70) 524(75)	506(64) 506(92)	430(14) 430(17)	412(28) 412(40)	 448(100)
2	706(25) 598(34) 580(36)	670(17)	598(100)	490(42) 490(82)	508(17) 508(13)	580(46) 580(26)	562(95) 562(100)	472(14) 472(26)	454(27) 454(36)	 490(100)
3	786(29) 662(18) 644(23)	750(23)	662(100)	538(18) 538(12)	556(9)	644(21) 644(24)	626(54) 626(100)	520(4)	502(5)	 538(100)
4	776(22) 654(35) 636(95)	740(44)	654(100)	532(15) 532(61)	550(13) 550(22)	636(42) 636(39)	618(50) 618(100)	514(14) 514(25)		 532(100)
5	861(20) 722(51)	825(27)	722(100)			704(49) 704(46)	686(17) 686(100)			
6	694(42) 600(21)		600(100)	506(88) 506(74)	524(96) 524(100)					
7	778(39) 670(12)		670(96)	562(100) 562(100)	580(37) 580(40)					
8	874(53) 750(30)		750(100)	626(28) 626(100)	644(11) 644(37)					
9	862(62) 740(21)		740(100)	618(21) 618(100)	636(57) 636(46)					
10	934(90)		795(100)	656(11)	674(27)					

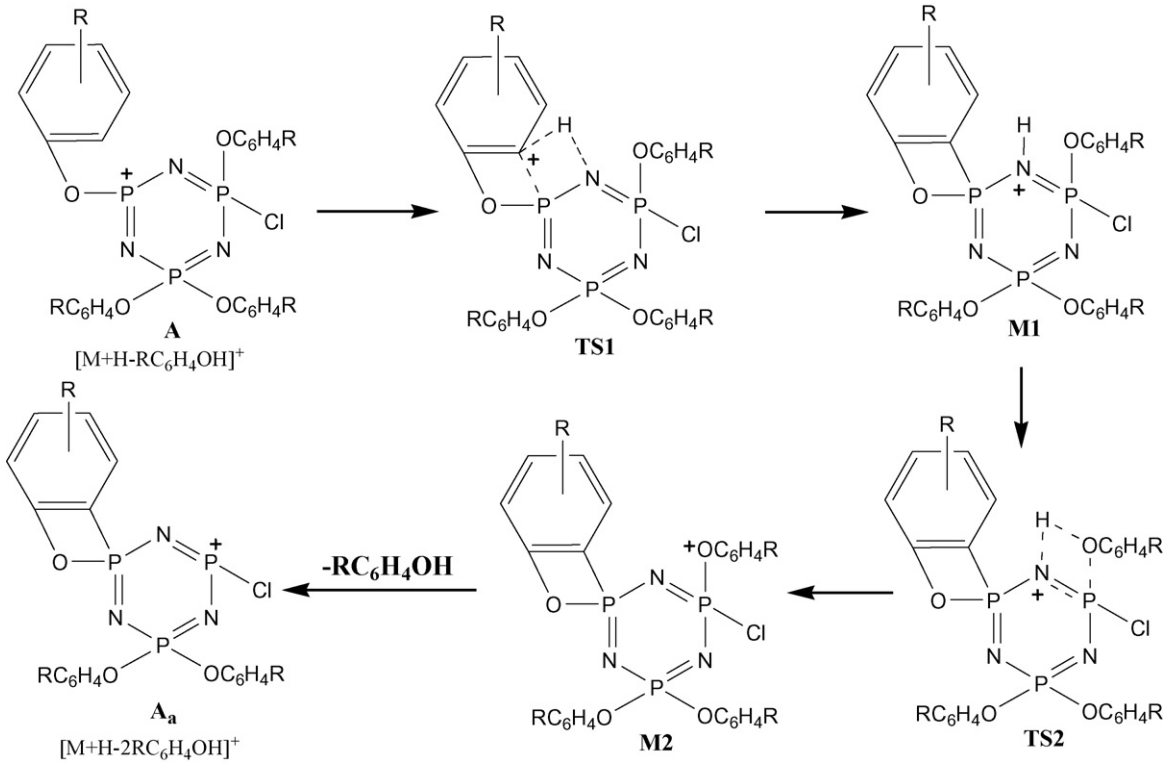
B = $[M+H-HCl]^+$; A = $[M+H-RC_6H_4OH]^+$; A_a = $[M+H-2RC_6H_4OH]^+$; A_b = $[M+H-RC_6H_4OH+H_2O-RC_6H_4OH]^+$; A_c = $[M+H-RC_6H_4OH-18\,Da]^+$; A_d = $[M+H-RC_6H_4OH-HCl]^+$; A_e = $[M+H-RC_6H_4OH+H_2O-RC_6H_4OH-HCl]^+$; A_f = $[M+H-2RC_6H_4OH-HCl]^+$; A_c-1 = $[M+H-RC_6H_4OH-18\,Da+H_2O-RC_6H_4OH]^+$.

sequently yields the more stable ion A_b. So, the source of the water molecule is key for explaining the formation of the ion A_b. It has been reported that the water molecule required for the hydrolysis reaction is presumably present in the ion trap [32]. To verify the product ion, high-resolution FTICR-MS for the compound **1** as a representative is performed. In the spectra, the ions A and A_b at *m*/*z* 542.0358 ($[M+H-PhOH]^+$, $C_{24}H_{20}ClN_3O_4P_3^+$) and 466.0018 ($[M+H-PhOH+H_2O-C_6H_5OH]^+$, $C_{18}H_{16}ClN_3O_4P_3^+$), respectively, are observed as shown in Table 2. The results of high-resolution FTICR-MS experiment definitely show that our supposition is reasonable.

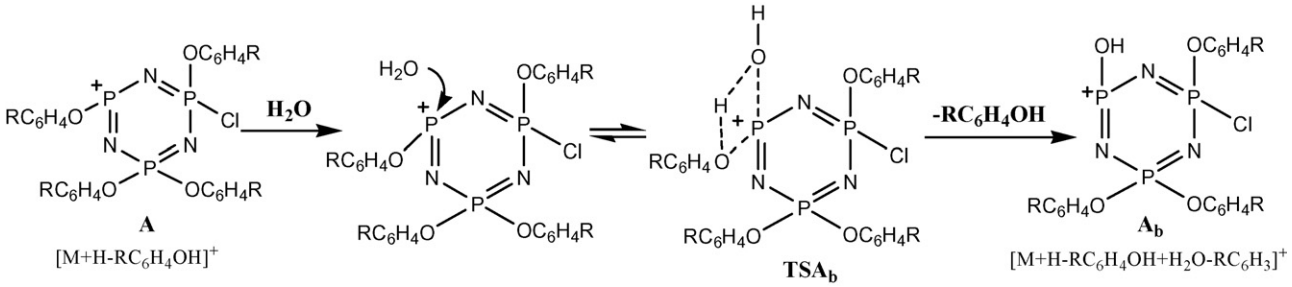
However, there is an unexpected ion A_c $[M+H-RC_6H_4OH-18\,Da]^+$, which is found not only in ESI-MS^2, but also in ESI-MS^3 (Table 1). According to ESI-MS^n, the ion A_c appar-



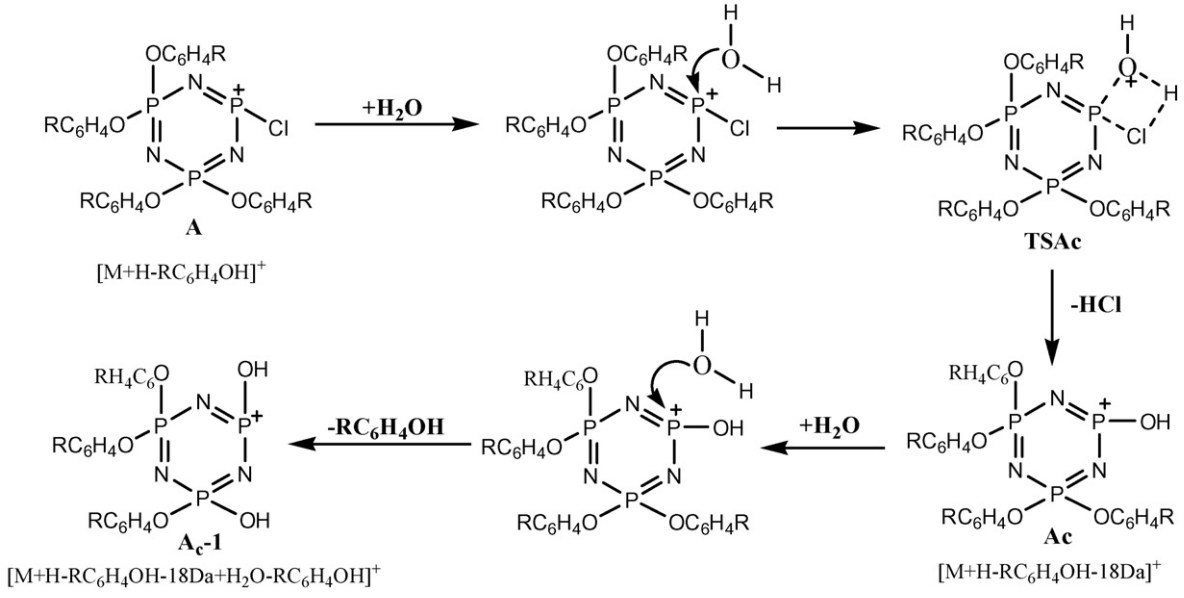
Scheme 2. Fragmentation pathways of **1**–**5**.



Scheme 3. Proposed mechanism of intramolecular electrocyclic ring closure for the A_a of **1**–**5**.



Scheme 4. Proposed hydrolysis mechanism for the A_b of **1**–**5**.



Scheme 5. Proposed hydrolysis mechanism for the A_c of **1**–**5**.

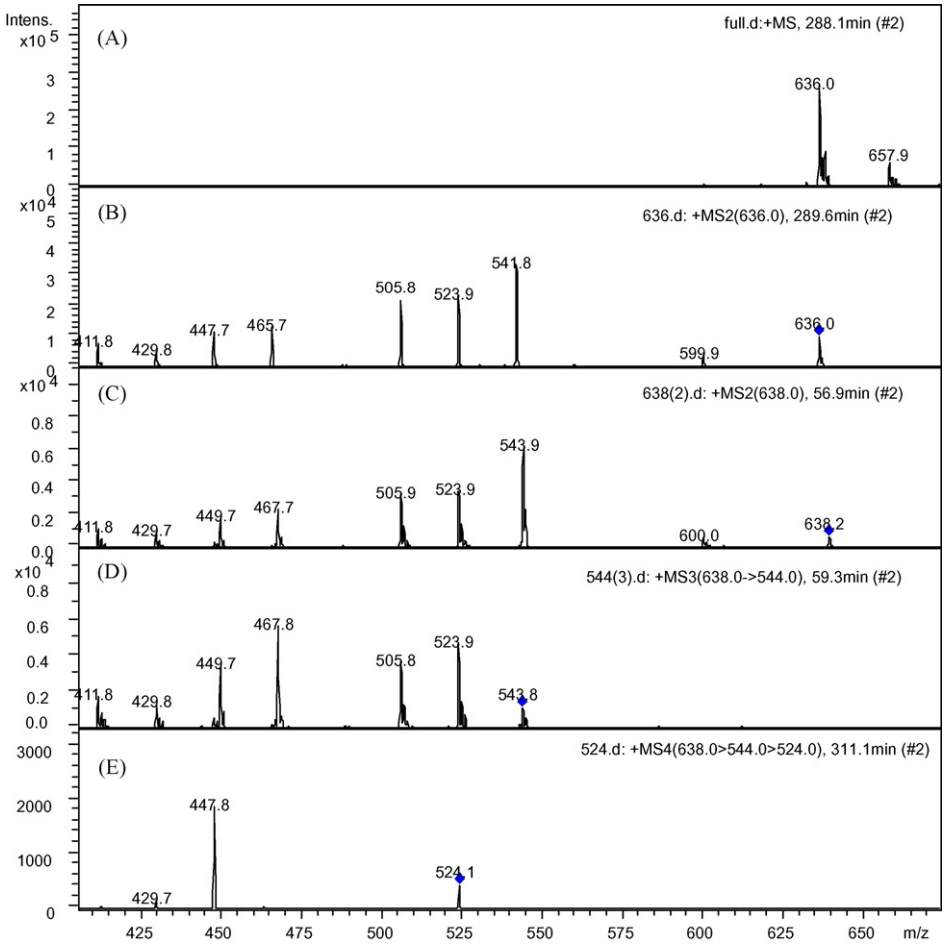
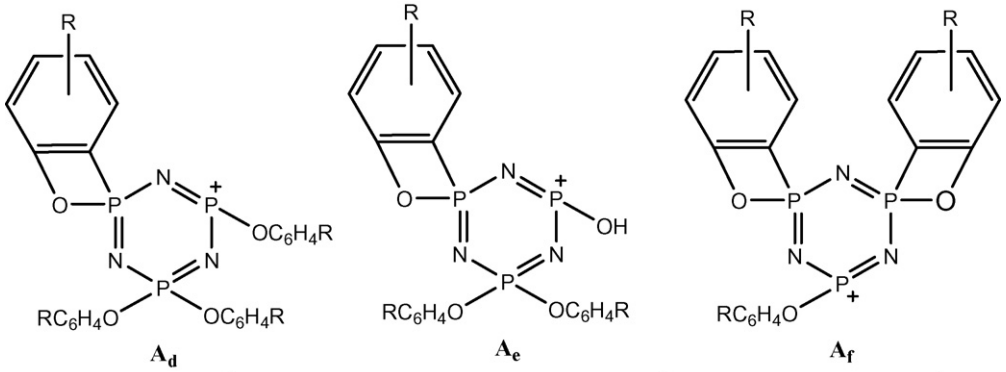


Fig. 2. MS^n of the compound **1**. (A) Full MS; (B) MS^2 of $[M+H]^+$ at *m*/*z* 636; (C) MS^2 of $[M+H]^+$ at *m*/*z* 638(^{37}Cl); (D) MS^3 of the ion at *m*/*z* 544(^{37}Cl); (E) MS^4 of the ion at *m*/*z* 524.



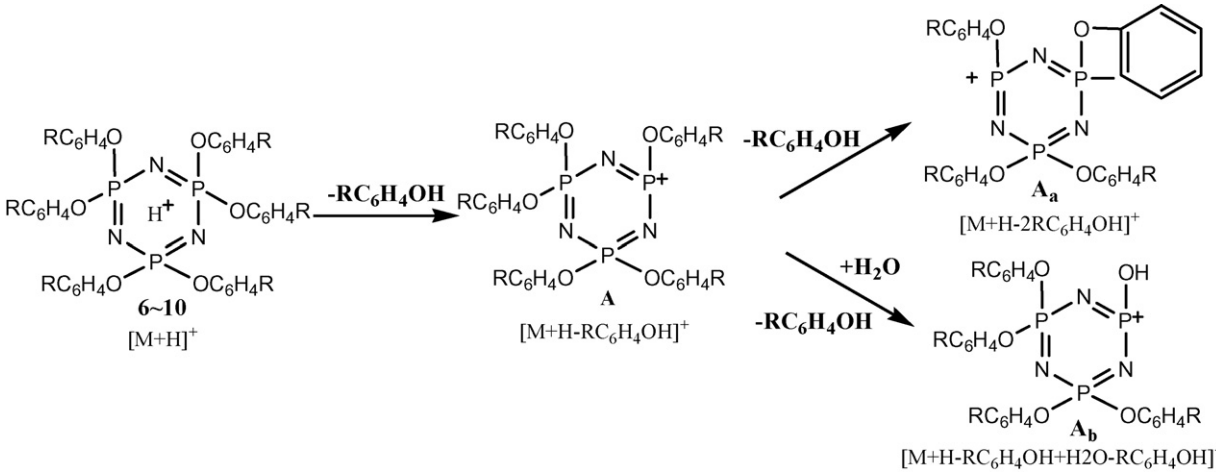
Scheme 6. Probable structures for the fragmentation ions A_d, A_e and A_f of **1**–**5**.

Table 2
High-resolution mass spectral data for the main ions of **1**[a].

Ion species	Theoretical mass (*m*/*z*)	Measured mass (*m*/*z*)	Relative error (ppm)
$[M+H]^+$	636.0768	636.0770	0.3
$[M+H\text{-}PhOH]^+(A)$	542.0350	542.0358	0.6
$[M+H\text{-}2PhOH]^+(A_a)$	447.9931	447.9932	0.2
$[M+H\text{-}PhOH+H_2O\text{-}C_6H_5OH]^+(A_b)$	466.0037	466.0018	4.1
$[M+H\text{-}PhOH\text{-}18]^+(A_c)$	524.0689	524.0702	2.5
$[M+H\text{-}PhOH\text{-}HCl]^+(A_d)$	506.0583	506.0569	2.8

[a] Obtained with ESI-MS in the positive ion mode.

ently results from the expulsion of a neutral fragment of mass 18 Da from the ion A $[M+H\text{-}RC_6H_4OH]^+$. A possible structure of the ion A_c is proposed in Scheme 5. The formation of the ion A_c could also possibly involve a hydrolysis reaction. With the oxygen atom in water attacking phosphonium center in the ion A, an intermolecular hydrogen bond (O–H···Cl) might be simultaneously formed to produce the transition state TSA_c $[M+H\text{-}RC_6H_4OH+H_2O]^+$. Elimination of an HCl molecule from the ion TSA_c might then yield the more stable ion A_c $[M+H\text{-}RC_6H_4OH+H_2O\text{-}HCl]^+$. The ion A_c might subsequently hydrolyze to form the ion $[A_c+H_2O]^+$, which can further fragment into the ion $[M+H\text{-}RC_6H_4OH+H_2O\text{-}HCl+H_2O\text{-}$



Scheme 7. Fragmentation pathways of **6**–**10**.

$RC_6H_4OH]^+$ (assigned as the ion A_c-1) by loss of a RC_6H_4OH molecule.

To further verify the structures proposed above, the compound **1** serves as an example and was interrogated in detail using techniques of isotopic selection and high-resolution FTICR-MS. ESI-MS^n is carried out by selecting the ^{37}Cl isotope at *m*/*z* 638 (Fig. 2A, C, D and E), in contrast to the typical ESI-MS/MS experiment that selects the ^{35}Cl isotope at *m*/*z* 636 (Fig. 2B). This experiment indicates that there is a chlorine atom in the precursor ion. The ion A_a at *m*/*z* 544 (selected isotope ^{37}Cl), an MS^2 product ion from the precursor ion, is 2 Da higher in mass than the corresponding ion at *m*/*z* 542 (the isotope ^{35}Cl), which would indicate that there is a chlorine atom in its structure. However, isotopic ratio of the ion A_c at *m*/*z* 524 is the same as that of the corresponding signal when the ^{37}Cl precursor ion is selected, which contradicts the previous observation and would indicate that there is no chlorine atom in its structure. The ion A_c at *m*/*z* 524 is observed in the MS^3 product ion spectrum of the mass-selected ^{37}Cl isotope of the compound 1 (Fig. 2D). Finally, accurate *m*/*z* measurements of ions using FTICR-MS indicated that the exact mass of the ion A_c at *m*/*z* 524 is 524.0702, corresponding to the formula $C_{24}H_{21}N_3O_5P_3$ (calculated 524.0689; relative error 2.5 ppm) (Table 2). This value is consistent with and supports the proposed structures.

Following the rationale just presented, formation of the remaining fragment ions A_d, A_e and A_f is easily understood, and their structures are exhibited in Scheme 6. Elimination of an HCl molecule from the ion A yields the ion A_d, which is the similar to the formation mechanism of the ion A_a. The ion A_e is the probable result of hydration of the charged phosphonium center followed by eliminations of HCl and RC_6H_4OH. Similarly, the ion A_f probably involves in successive loss of RC_6H_4OH and HCl from the ion A.

In addition, a comparison of the ESI-MS^n fragmentation pathways of the penta- and hexa-aryloxycyclotriphosphazenes has been conducted. Compounds **6**–**10** have been prepared (Scheme 1), and analyzed by ESI-MS^n (Table 1). As shown in Scheme 7, the fragmentation pathways of the compounds **6**–**10** are similar to the compounds **1**–**5**. The base peak A, is also observed, originating from the elimination of a RC_6H_4OH molecule from $[M+H]^+$. The ion A fragments further into the ion A_a through elimination of a hydroxyl aromatic molecule, and hydrolysis to form the ion A_b, with an associated loss of a hydroxy aromatic molecule. These data would indicate that a hydrolysis reaction is a common fragmentation phenomenon in the aryloxycyclotriphosphazenes **1**–**10**.

4. Conclusions

In the paper, the main fragmentation pathways are elucidated in positive ESI-MS^n for penta- and hexa-substituted aryloxycyclotriphosphazenes. A unique hydrolysis mechanism, which involves water attacking a charged phosphonium center, with subsequent elimination of HCl or a hydroxy aromatic molecule, is the most common fragmentation phenomenon in the compounds **1**–**10**. However, in the ESI-MS^3 of them another novel fragment mechanism was revealed. An apparent intramolecular electrocyclic ring closure is observed, characterized by phosphonium ion attacking the *ortho*-position on the aromatic ring assisted by intramolecular hydrogen bonds (C–H···N=P). These observations may have some potential applications in the distinction between the mass spectra of penta- and hexa-substituted derivatives for hexachlorocyclotriphosphazenes.

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